IMPROVED TACK PMR

CONTRACT NAS 3-22026

R. A. BUYNY

OCTOBER 1981

Prepared for

NASA LEWIS RESEARCH CENTER.
2100 BROOKPARK ROAD,
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DEFENSE AND SPACE SYSTEMS GROUP

1. Report No. NASA CR-165432	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle "Improved Tack PMR"		5. Report Date OCTOBER 1981
		6. Performing Organization Code
7. Author(s) R. A. Buyny		8. Performing Organization Report No. 36805.6016.UT-00
9. Performing Organization Name and Address TRW, Inc. Defense and Space Systems Group One Space Park Redondo Beach, CA 90278		10. Work Unit No.
		11. Contract or Grant No. NAS 3-22026
12. Sponsoring Agency Name and Address National Aeronautic and Space Administration Washington, D. C. 20546		13. Type of Report and Period Covered Contractor Report
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

One reactive diluent and several high boiling solvents were investigated for providing long shelf life tack and drape to PMR polyimide prepreg materials. The most promising approach was to introduce dimethoxy ethyl ether (diglyme) to the normal methanol solvent. Compression and autoclave molding cycles were developed for the improved tack prepreg which provided up to 15% higher thermomechanical properties than conventional PMR-15 composites. Near the conclusion of this investigation, it was discovered that diglyme constituted a potential hazard because its auto ignition temperature is $464^{\circ}K$. Consequently, it was recommended that diglyme should not be used as a tackifier for PMR prepregs.

17. Key Words (Suggested by Author(s)) Tackifier Polyimide Composite Diglyme	18. Distribution Statement UNCLASSIFIED, UNLIMITED 4-23-84 per Shirley (Mollette Lewis)		
19. Security Classif. (of this report) UNCLASSIFIED	20. Security Classif. (of this page) UNCLASSIFIED	21. No. of Pages	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-C-168 (Rev. 10-75)

FOREWORD

This report was prepared by TRW Defense and Space Systems Group, Redondo Beach, California, under contract NAS3-22206, "Improved Tack PMR". The technical effort was performed between 27 July 1979 and 1 May 1981 under the sponsorship of the NASA/Lewis Research Center. Mr. Raymond D. Vannucci served as project engineer.

The initial screening studies of the program were conducted by TRW Equipment Group, Cleveland, Ohio. Mr. William Winters served as Program Manager and Mr. Paul Cavano was Principal Investigator and was in charge of all experimental activities.

The remainder of the technical effort was performed at TRW DSSG with Mr. R. W. Vaughan serving as Program Manager. Mr. R. A. Buyny served as Principal Investigator and was responsible for experimental and reporting activities. Additional technical contributions were made by Mr. M. K. O'Rell, Ms. L. Fraser, and Mr. K. Yates. Mr. William Winters provided valuable technical contributions as a Program Consultant for the technical effort accomplished at TRW DSSG.

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IMPROVED TACK PMR

by

R. A. Buyny

SUMMARY

This report is the final report document describing work performed by TRW Equipment Group and TRW Defense and Space Systems Group for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-22026. The technical work on this program was performed during the period of 27 July 1979 through 1 May 1981.

' The objective of this program was to investigate reactive and non-reactive compounds which would introduce longer duration (i.e., $\geq$ one month) tack and drape into PMR polyimide prepreg materials. Further, a promising tackifier candidate should not compromise the PMR-15 autoclave processing cycle commonly adopted at present by the trade [i.e., cure temperatures $\leq$ 589°K (600°F) and pressures $\leq$ 1.4 MPa (200 psia)] or initial or retained mechanical properties at 589°K (600°F).

In this program, one reactive diluent and several high boiling solvents were investigated as an approach to improve the handleability (i.e., tack, drape, etc.) of PMR-15 prepregs. It was determined that the most promising and simplistic method of introducing the desired tack into PMR-type prepregs was to add dimethoxy ethyl ether (diglyme) to the normal methanol solvent.

Compression and autoclave fabrication cycles were developed for the desired tacky prepreg which yielded composites possessing up to 15% higher thermo-mechanical properties than did composites prepared from the conventional PMR-15 prepreg. To ensure removal of the diglyme tackifier solvent, it was necessary to increase the dwell cycle and use a higher heat-up rate than normally employed by the trade to autoclave process PMR-15 composites.

Near the conclusion of this investigation, TRW discovered on a separate in-house study that diglyme constitutes a potential hazard because its auto-ignition temperature was found to be 464°K (375°) instead of the previously reported 811°K (1000°F). For this reason it is recommended that the use of diglyme as a tackifier compound for PMR-15 prepreg should not be considered further.

Details of the experimental work performed on this program was
presented throughout the remainder of this final report.

1.0 INTRODUCTION

This final report presents the work accomplished by TRW Equipment Group and TRW Defense and Space Systems Group for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-22026, during the period of 27 July 1979 through 1 May 1981. This effort involved the definition and evaluation of methods to improve the handleability characteristics, *i.e.*, tack and drape, of PMR-15 prepregs. Prepregs utilizing the most promising methods of improving the tack and drape of the PMR system were then fabricated into laminates to demonstrate the relative processability of the improved tack PMR system.

Over the last several years, PMR composites have been accepted in the industry and are currently used for a diversified list of applications. The basic prepreg material is available commercially from several vendors. The ease of processing of these prepregs has been demonstrated by the large number of high quality hardware items fabricated from these systems.

While there are many advantages of the PMR addition polyimide system in comparison to the conventional condensation polyimide systems, one characteristic of the PMR system has limited its application. This characteristic is the relatively short prepreg tack life. The PMR system relies on the retention of some of its carrier solvent, methanol, to provide tack to the prepreg. Since methanol has a relatively low molecular weight and is quite volatile, it diffuses and evaporates from single plies of prepreg very quickly. Usually enough residual methanol leaves the prepreg within twenty four hours under ambient conditions that the prepreg loses all of its tack.

The most promising approach identified on this program to extend the tack life of PMR prepregs involved the incorporation of an additional less volatile fugitive carrier solvent into the conventional PMR-15 formulation. The ratio of the fugitive solvent, dimethoxy ethyl ether (diglyme), to the methanol solvent was one to four. By performing this simple formulary modification and preparing both woven and unidirectional prepregs using a

conventional resin solution impregnation technique, it was possible to realize adequate handleability and tack after exposure under ambient conditions for fourteen days.

The processability of the improved tack PMR prepregs was evaluated through the fabication of various sized laminates. Fabrication was accomplished by using either compression or autoclave molding techniques. For comparative purposes several laminates were fabricated using the conventional PMR-15 formulation, *i.e.*, the same lots of monomers were employed but diglyme was omitted. It was observed that the improved tack PMR prepregs exhibited somewhat lower resin flow during molding than the conventional PMR-15 prepregs. Cursory examination of the melt viscosity behavior of imidized powder of these two systems showed the improved tack PMR prepolymer to be substantially more viscous. In spite of this change in the rheology of the improved tack PMR system it was possible to mold high quality, low void laminates. In addition, the mechanical properties of the improved tack PMR laminates were equivalent to, or higher than, those of the PMR-15 control laminates. This was true both before and after exposure of these laminates to isothermal aging at $588^{0}K$ ($600^{0}F$).

An excess of the carrier solvent was used during most of the program for the solution impregnation of the fibers. However, additional prepreg was also prepared by using hot melt coating techniques. Laminates fabricated from this material, both by compression and autoclave molding techniques, exhibited processability and mechanical and physical properties comparable to the laminates fabricated from solution impregnated prepreg. The tack life of the hot melt prepreg was also extended to about fourteen days. This hot melt PMR formulation employed the conventional monomeric ingredients and enough diglyme to afford a pliable, semi-solid and tacky resin at room temperature. Only diglyme was used as the carrier solvent.

During the concluding stages of the technical effort described herein, an incident occurred in another experimental program at TRW which precludes the use of diglyme as a tackifier solvent for PMR-15 prepreg. Specifically, in this in-house TRW sponsored program, on a different class of polyimides, it was observed that diglyme self-ignited at an evaporation temperature of $477^{O}K$ ($400^{O}F$). During the investigation of this incident, it was learned from a manufacturer that the accepted auto-ignition temperature of diglyme of $811^{O}K$ ($1000^{O}F$) was being treated as suspect. Very recently, TRW was informed by the manufacturer that the auto-ignition temperature of diglyme was established to be $464^{O}K$ ($375^{O}F$). Because of this drastic reduction in the auto-ignition temperature of diglyme, it is recommended that diglyme not be used as a tackifier or solvent carrier for polyimides in general and PMR-15 in particular.

This report is divided into six sections covering the program technical efforts:

    (1) Tackifier Screening Studies

    (2) Compression Molding Process Development Using Woven Prepreg

    (3) Compression Molding Process Development Using Unidirectional Prepreg

    (4) Autoclave Molding Process Development

    (5) Conclusions and Recommendations.

    (6) Appendices

2.0 TACKIFIER SCREENING STUDIES

In selecting candidate tackifiers for the program, the following limitations were observed as goals:

- Any additive used shall not adversely affect processing parameters or ease of fabricability including curing conditions

- The additive should be liquid at room temperature and of low vapor pressure

- The mechanical properties of the resulting composite shall not be reduced at room temperature or at elevated temperature for extended exposure times

- It should be compatible with PMR monomers and prepolymer

- Additive shall have minimum toxicity

- The basic stoichiometry of the PMR-15 system shall not be altered in such a way so as to affect composite performance

- Formulation changes shall be applicable to both solution and hot melt impregnation techniques.

The two general approaches considered for enhancing drape and tack of PMR-15 prepregs were: (1) the use of a less volatile solvent and (2) the use of a liquid reactive diluent.

The primary requirements for the solvent additives include high solvency, low toxicity and non-reactivity with the PMR monomers. Also, the volatility of the additive should be such as to be easily expelled in the early stages of the cure cycle. The two step cure of the PMR system affords an excellent opportunity for the use of a fugitive additive system. Cure cycles generally employ an imidization step in the range of 394-477°K (250-400°F) under low pressure or in a circulating air oven followed by cure at 573-603°K (575-625°F). Selecting an additive that boils or becomes volatile in the range of 394-477°K while possessing the other criteria should assure quantitative expulsion in the imidization. More specifically, the higher the boiling point the longer out-time might be expected, although too high a boiling point, say near the 477°K (400°F) maximum PMR imidization temperature, might not assure full elimination of the added solvent and could cause porosity in the final composite. A more appropriate boiling range was thus considered to be 394-450°K (250-350°F).

There are, of course, many solvents that might be considered, but by using the selection criteria noted above and eliminating solvents with propensities for side reactions with the monomeric PMR ingredients, four solvents were chosen for examination on this program. These were, in addition to the methanol control, ethanol, n-butanol, butyl ether and diglyme. The physical properties of these candidate solvents are shown in Table 1.

Another approach to the extension of tack retention time is one of adding a fourth monomer or substituting one monomer for a portion of the three making up PMR-15. The additional monomer would be a liquid material that would not evaporate at room temperature, thus leaving a moist or tacky prepreg. As opposed to the fugitive carrier solvent method, this monomer would react during the cure process so that it would not volatilize into a void producing gas.

It has been suggested (Reference 1) that an olefinic double bond in the fourth monomer might provide a mechanism for polymerization with the PMR-15. There are obviously numerous candidates which could be used in this manner, as a reactive diluent. However, very few would be compatible with the PMR imidized prepolymer. A notable exception should be nadic methyl anhydride (NMA) shown below. Due to its anhydride functionality,

Nadic Methyl Anhydride
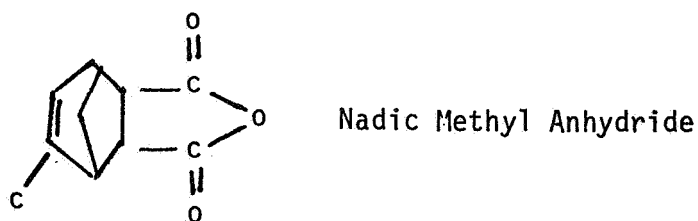
this monomer should be incorporated into the PMR backbone during the condensation stages of processing and thus should remain compatible with the high molecular weight prepolymer. This was the only monomer evaluated as a reative diluent, since it was the most likely one to be compatible with PMR chemistry. In addition, NMA was selected because it allows the

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Table 1. PROPERTIES OF CANDIDATE SOLVENTS

	Dimethoxy Ethyl Ether (Diglyme)	Methanol	Ethanol	Butyl Ether	n-Butanol
Molecular Weight	134	32	47	130	74
Boiling Point, °F	324	149	145	284	243
Freezing Point, °F	-83	-144	-165	-144	-121
Vapor Pressure (68°F) mm Hg	3	97	44	4.8	4
Density, g/cc	0.947	0.793	0.789	0.769	0.811
Dielectric Constant	5.8	--	--	--	16.1
Dipole Unit, Denbye Units	2.0	--	--	--	--
Flash Point (Closed Cup), °F	158	57	57	77	84
Ignition Temperature, °F	(4)	878	799	--	693
Toxicity					
Threshold Limit Value[1], ppm	--	200	1000	None	50
Orl-rat[1], LD_{50}[2], g/kg	7	13	14	11	4.4
Orl-humn[1], LDL_O[3], g/kg	--	0.34	0.50	--	0.5

(1) Reference "Registry of Toxic Effects of Chemical Substances," NIOSH, 1977 Edition.

(2) The lethal dose to rats given orally that will cause death to 50% of the population.

(3) The lowest dose known to have cuased death to humans when taken orally.

(4) Currently under investigation by the Ansul Corporation.

use of a liquid monomer with the minimum adjustment of standard stoichio-
metry. The material represents a low cost, readily available monomer that
is in everyday use as a curing agent for epoxy resins. Its liquid nature
also seems appealing for use with high monomer concentration solutions for
use with hot melt impregnation techniques.

A logical extension of the use of either added reactive diluents or
an added solvent is the combination of these two approaches to perhaps
achieve a synergystic effect. For this reason, a combination of diglyme
solvent with nadic methyl anhydride was evaluated.

In summary then, the following modifications to the standard PMR were
examined in the first task of the program.

a)   Standard PMR-15 with methanol (control).

b)   Diglyme as a solvent.

c)   Butyl ether as a solvent.

d)   n-Butanol as a solvent.

e)   Nadic methyl anhydride as a reactive diluent.

f)   Nadic methyl anhydride with diglyme in combination.

Ethanol was not included in this list of candidate tackifier systems.
However, it was reserved for use as a carrier solvent, of less volatility
than methanol.

To evaluate these systems to improve the tack of PMR prepregs,
solutions containing 50% w/w of uncured resin solids were prepared from the
conventional PMR-15 monomers, methanol and selected solvent and/or reactive
diluent. Celion C-3000 fabric was then coated with these solutions. The
resultant prepregs were then evaluated for tack drape and retention of
volatile matter. Systems exhibiting the most desirable handleability and
tack life were selected for evaluation of their bulk resin properties.
These tasks are described in the following sections. From these studies
two systems were selected for composite processing evaluation.

2.1 FORMULARY MODIFICATIONS

Solutions of the candidate improved tack PMR systems were prepared by using the ratio of ingredients shown in Table 2. The fugative solvents were substituted, on a weight basis, for 20% of the normal weight of the carrier solvent. The reactive diluent, NMA, was employed in a 0.4 to 1.6 ratio with NE. The BTDE was prepared by refluxing the dianhydride, BTDA, with an excess of alcohol for a period of one hour, after the clearing of the initial suspension. Either anhydrous methanol or ethanol was employed. All esterifications were performed at a 50% w/w solids concentration, based upon the final diester weight. After the BTDE had cooled, it was mixed with a previously prepared 50% w/w solution of MDA, NE, methanol and fugitive solvent. NMA was added at this point in the noted formulations. All solutions were prepared in a three neck flask equipped with a stirring motor and paddle, thermometer and reflux condenser.

2.2 PREPREG STUDIES

All prepregs examined in these screening studies and subsequent preliminary composite processing studies (Sections 3 and 5) were prepared from a single lot of woven C-3000 fabric. This material had an 8-Harness Satin construction with 23x22 tows per inch in the warp and fill directions, respectively. The fibers were sized, at approximately a 1% w/w level, with an epoxy compatible material. Typical composite properties of this reinforcement with either Fiberite 934 epoxy or PMR II matrices are given in Table 3.

Fiber impregnation was achieved by spreading a calculated amount of 50% w/w solution onto a preweighed section of the C-3000 fabric. By using a teflon doctor blade it was possible to attain resin contents that were reproducible to $\pm$ 1.5%. Standard procedure was to make up the prepreg, leave the material uncovered for 24 hours and then perform tack, drape and volatile content tests.

These tests, the procedures for which are given in Appendix A, were used to define the useful shelf life of prepregs. For aging at ambient conditions, prepreg was allowed to lay with the top side uncovered on a laboratory bench with the release paper or film in place on the bottom side. Just prior to testing, the release paper was removed from both strips

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Table 2. CANDIDATE IMPROVED TACK PMR FORMULATIONS

Monomer	Mol. WT	Formulation (No. of moles/p.b.w.)					
		1	2	3	4	5	6
NE (5-Norbornene-2,3-dicarboxylic acid monomethyl ester)	196.1	2.000/397.4	2.000/392.4	2.000/392.4	2.000/392.4	1.600/313.8	1.600/313.8
NMA (Nadic methyl anhydride)	164.2	-	-	-	-	0.400/65.7	0.400/65.7
BTDE (Dimethyl ester of 3,3',4,4' benzophenone tetra carboxylic acid(1))	386.3	2.087/806.2	2.087/806.2	2.807/806.2	2.087/806.2	2.087/806.2	2.087/806.2
MDA 4,4' Methylene dianiline	198.3	3.087/612.2	3.087/612.2	3.087/612.2	3.087/612.2	3.087/612.2	3.087/612.2
Total weight, uncured resin solids		1811	1811	1811	1811	1798	1798
Methanol		1811	1449	1449	1449	1798	1438
Diglyme			362	362			
n-Butanol					362		
t-Butyl ether							360

(1) Prepared by esterification of 2.087 (672.4 p.b.w.) of benzophenone tetracarboxylic acid dianhydride in methanol.

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Table 3. CELION-3000 FABRIC COMPOSITE PROPERTIES
AS REPORTED BY VENDOR (REF. 2)

Fabric: Fiberite Style W-1133, 24 x 23 8 Harness Satin

Composite: 65 volume percent Celion 3000 in Fiberite 934 epoxy resin.

	Warp		Fill	
Flex Strength, MPa (Ksi)	943	(136.7)	903	(131)
Flex Strength, MPa (Ksi) @ 450°K (350°F)	808	(117.2)	696	(100.7)
Flex Modulus, GPa (Msi)	76	(11.0)	72	(10.5)
Flex Modulus, GPa (Msi) @ 450°K (350°F)	74	(10.7)	70	(10.1)
ILSS, MPa (Ksi)	67	(9.7)	68	(9.9)
ILSS, MPa (Ksi) @ 450°K (350°F)	49	(7.1)	46	(6.7)
Tensile Strength, MPa (Ksi)	643	(93.2)	593	(86)
Tensile Modulus, GPa (Msi)	79	(11.4)	72	(10.5)

Celion 3000 - High Strength carbon fiber with 3000 filaments per strand.
The above properties were obtained on autoclave cured laminates by Fiberite Corporation.

TYPICAL CELION 3000/PMR II POLYIMIDE COMPOSITE PROPERTIES				
	293°K (73°F)		588°K (600°F)	
	Unidirectional	Fabric	Unidirectional	Fabric
Flex Strength, MPa	1520 - 2000	793	900 - 1000	552
(Ksi)	(220 - 290)	(115)	(130 - 145)	(80)
Flex Modulus, GPa	121 - 145	62	-	-
(Msi)	(17.5 - 21)	(9)	-	-
Interlaminar Shear Strength MPa	97 - 123	48	48 - 55	41
(Ksi)	(14 - 17.8)	(7)	(7 - 8)	(6)
Celion 3000 - High Strength carbon fiber with 3000 filaments per strand				

and release paper side (wet) of one strip was joined with the open (dry) side of the other strip to form the lap joint. It was felt that this simulates lay-up conditions of a composite component.

Figures 1 through 6 display the tack, drape and volatile content data collected on each of the formulations listed in Table 2. Figure 1 shows the behavior of the unmodified, control system and, as can be seen, the tack values drop rapidly with time. At the end of six days, one sample replicate had a value of 2 psi, but the average was below 1 psi. The NMA system (Figure 5) provided little extension of this time. Figures 2 and 6 show considerable improvement in tack retention with either the diglyme alone and the NMA with diglyme. In each case, testing was terminated because of complete consumption of the test prepreg. Note also that both of the systems containing diglyme maintained a higher volatile level and drape characteristics for a correspondingly longer time. Figure 3 shows the data collected on the n-butanol system. The butanol addition did show improved performance, but the tack values were, for the most part, consistently lower than the diglyme system. The n-butyl ether tackifier (Figure 4) imparted very little improvement in tack life.

Based on these data, it appears that diglyme quality increases the tack of PMR systems. N-butanol increases it somewhat, and n-butyl ether and NMA have very little effect upon tack. In addition n-butanol is relatively toxic, with a threshold limit of 50 ppm, and has a very pungent odor. These factors and its marginal improvement upon tack life combined to eliminate n-butanol as a viable choice as a suitable tackifier.

Thus, as a result of these prepreg screening studies, diglyme appeared to be the only viable additive to impart tack to PMR systems. Since ethanol is also a viable solvent for PMR resins, it was decided to evaluate a single fugitive solvent and two carrier solvents, methanol and ethanol as improved tack PMR solvent systems. It was anticipated that the reduced volatility of the ethanol/diglyme mixture might enchance the tack characteristics of this system.

Figure 1. Change in Prepreg Characteristics with Time
Formulation 1: Control Prepreg

Figure 2. Change in Prepreg Characteristics with Time
Formulation 2: Diglyme (20 w/o)
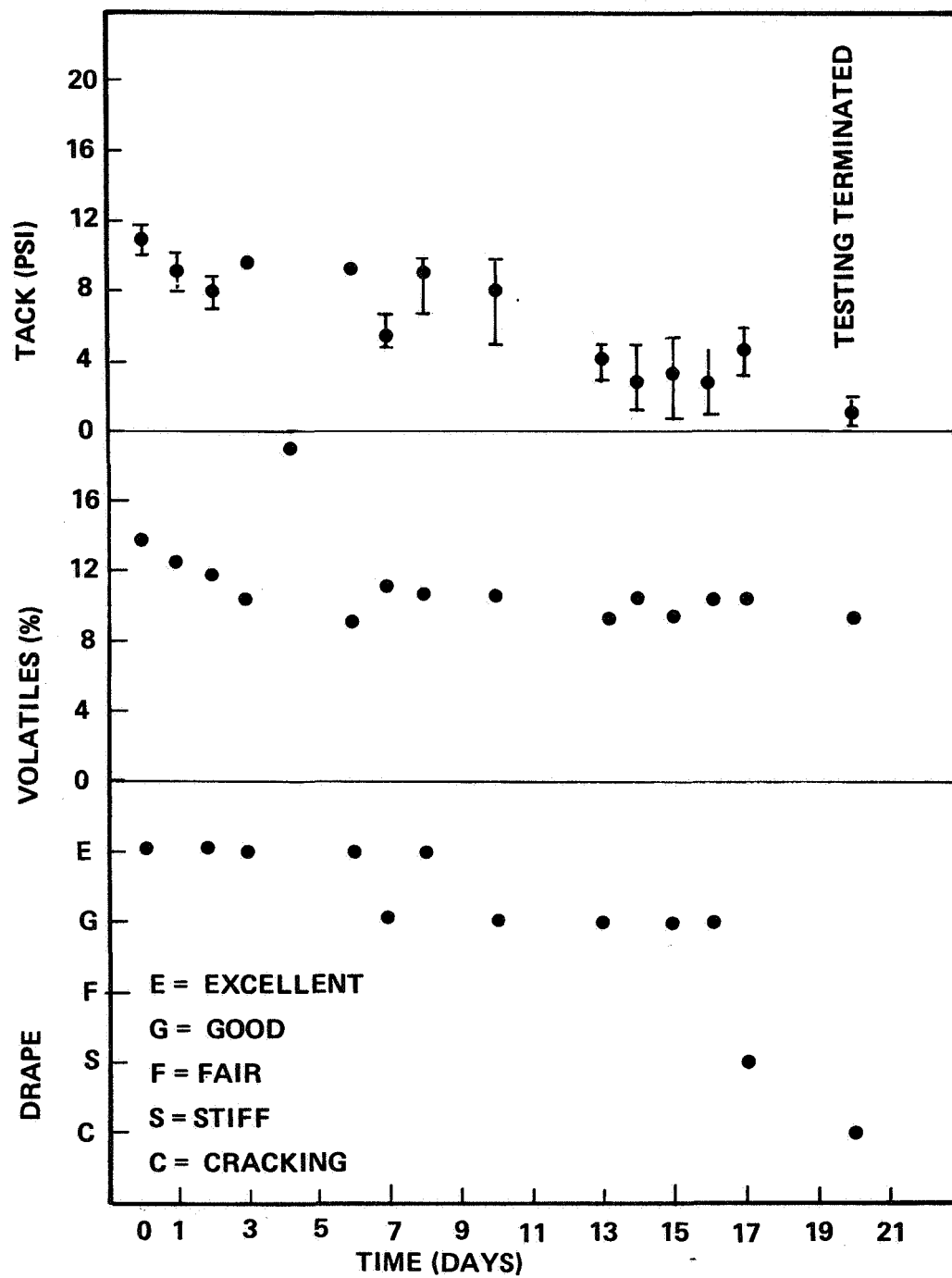
Figure 3: Change in Prepreg Characteristics with Time
Formulation 3: n-Butanol (20 wa)
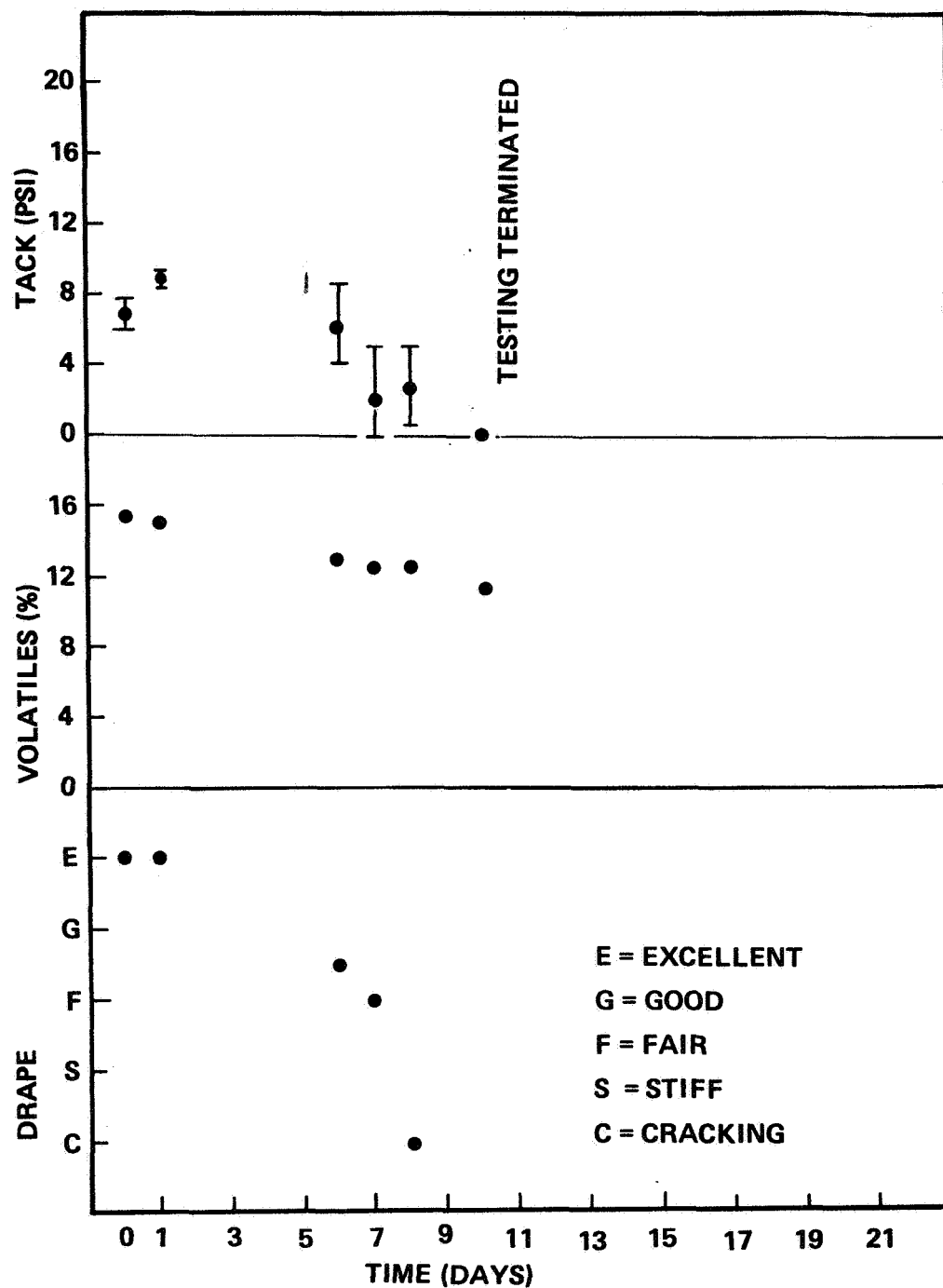
Figure 4:   Change in Prepreg Characteristics with Time
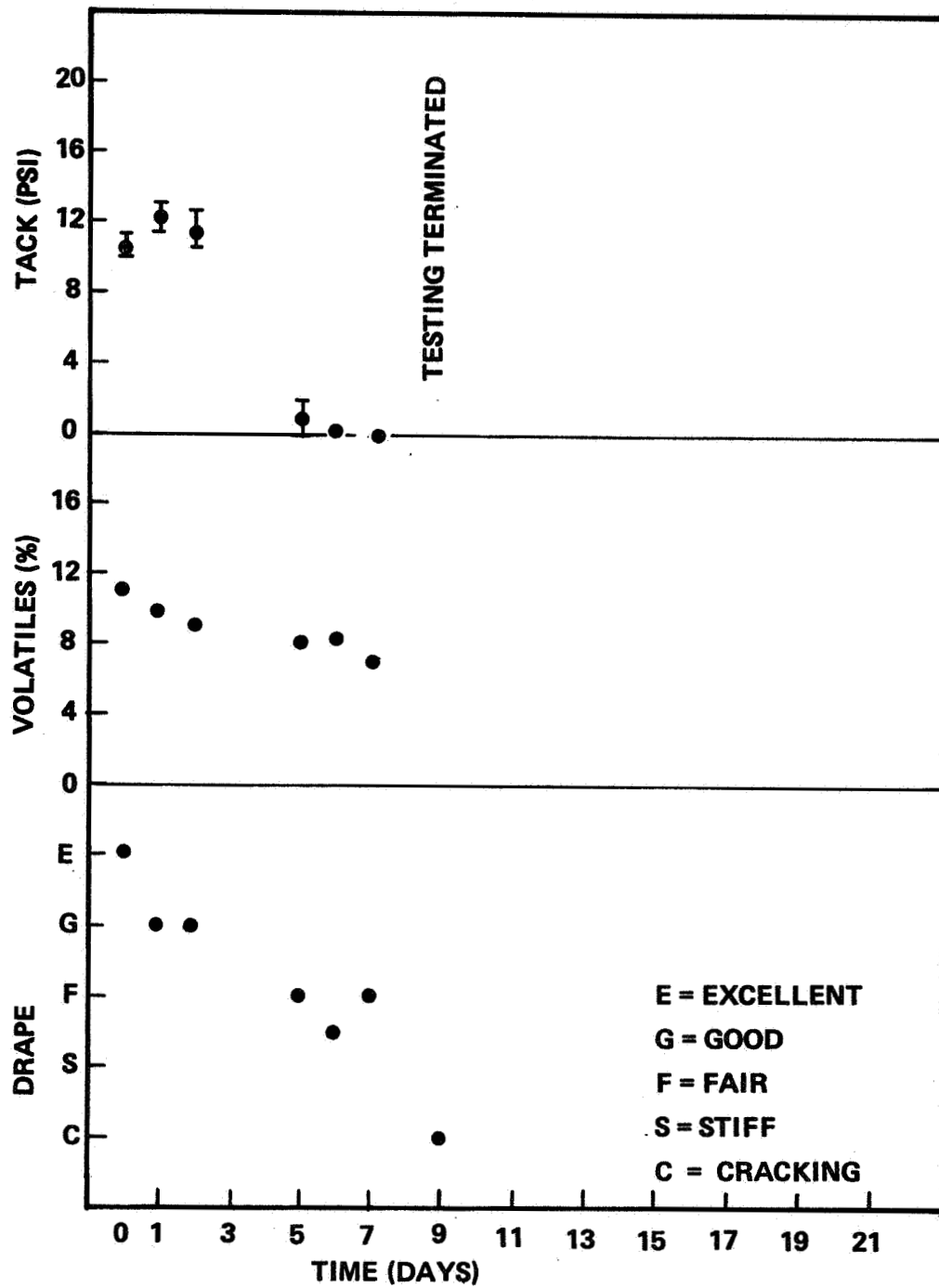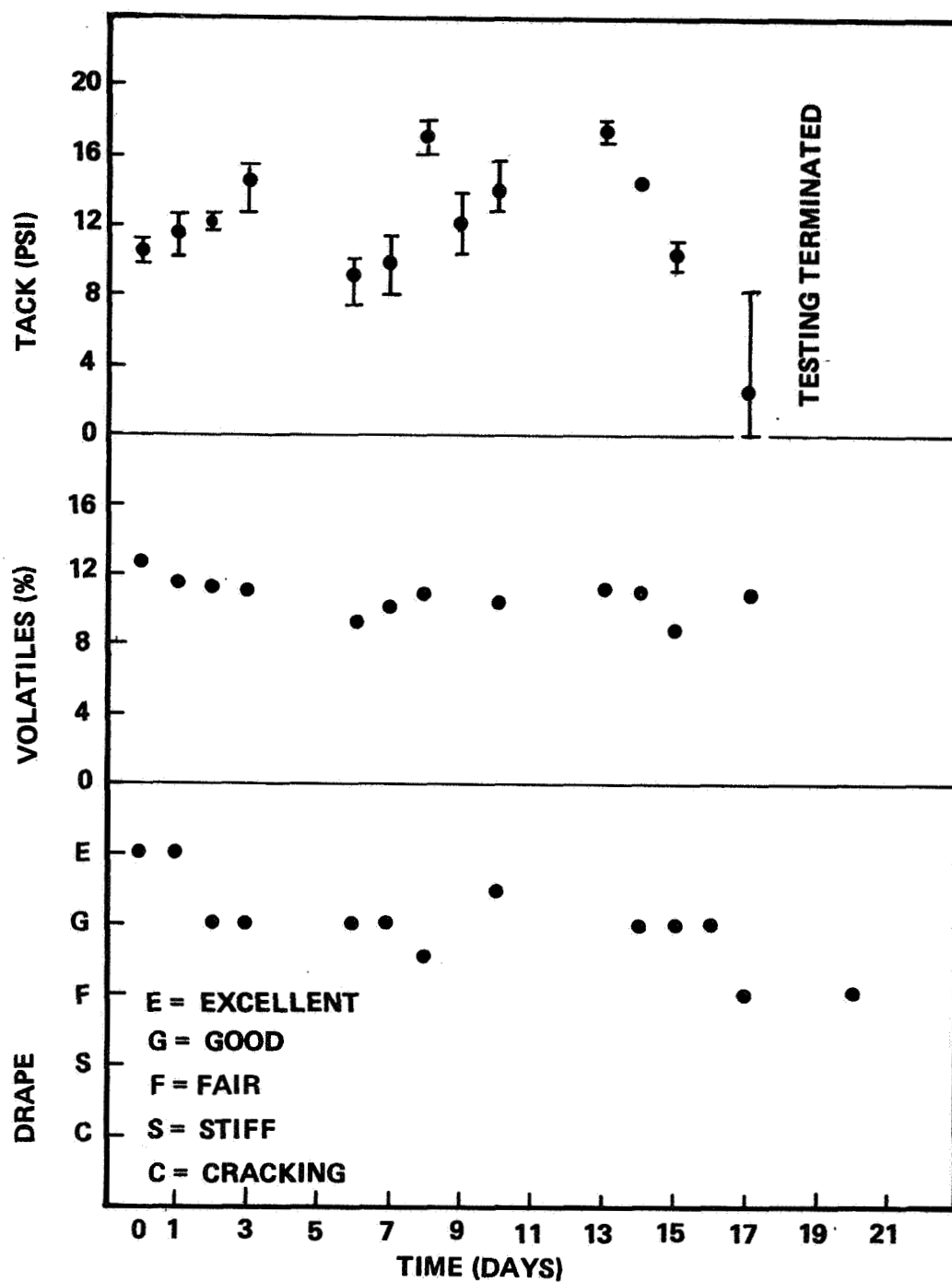Formulation 4:   1-Butyl Ether (20 w/o)
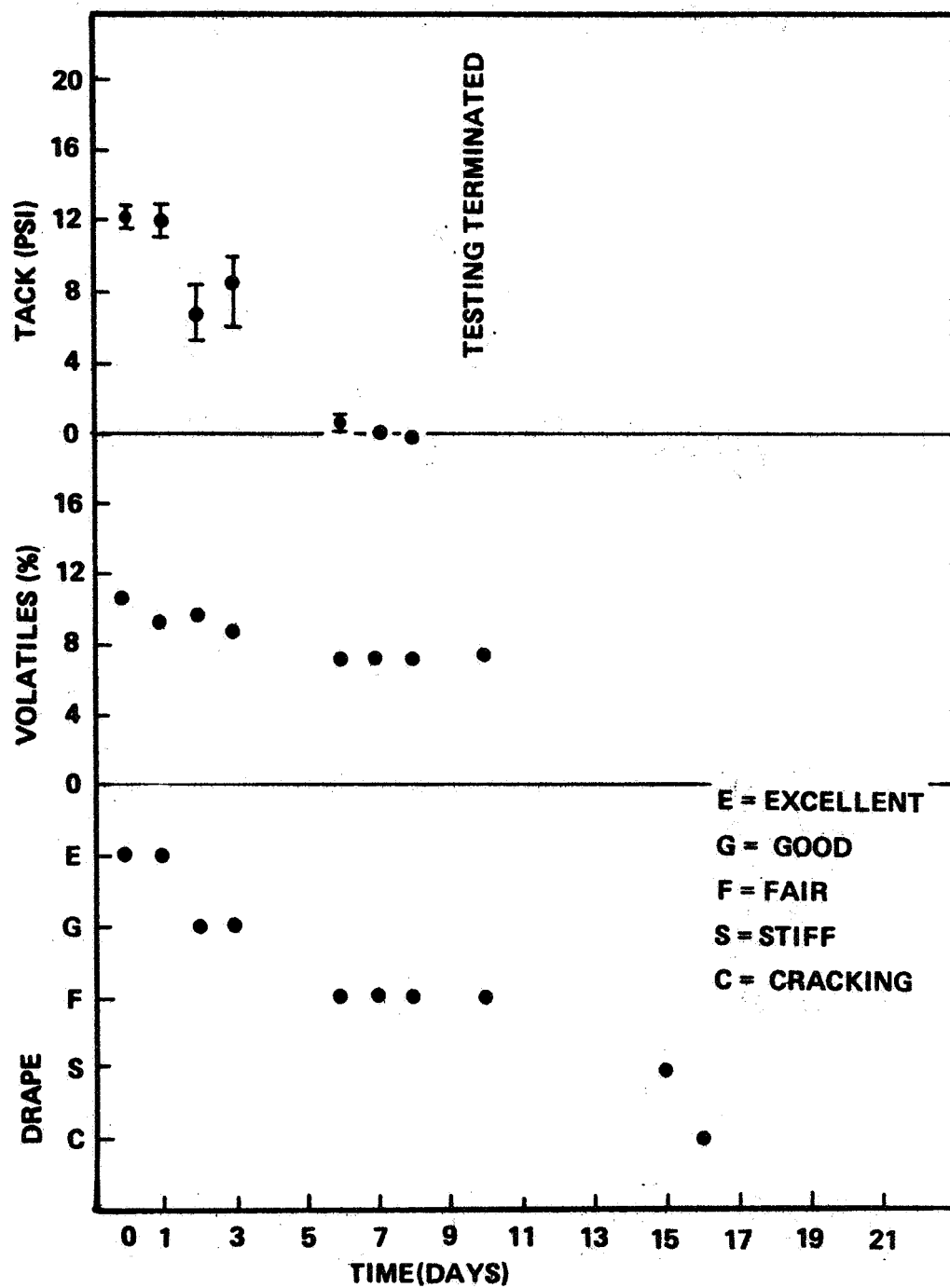
Figure 5:   Change in Prepreg Characteristics with Time
Formulation 5:   NMA (0.4 mole)
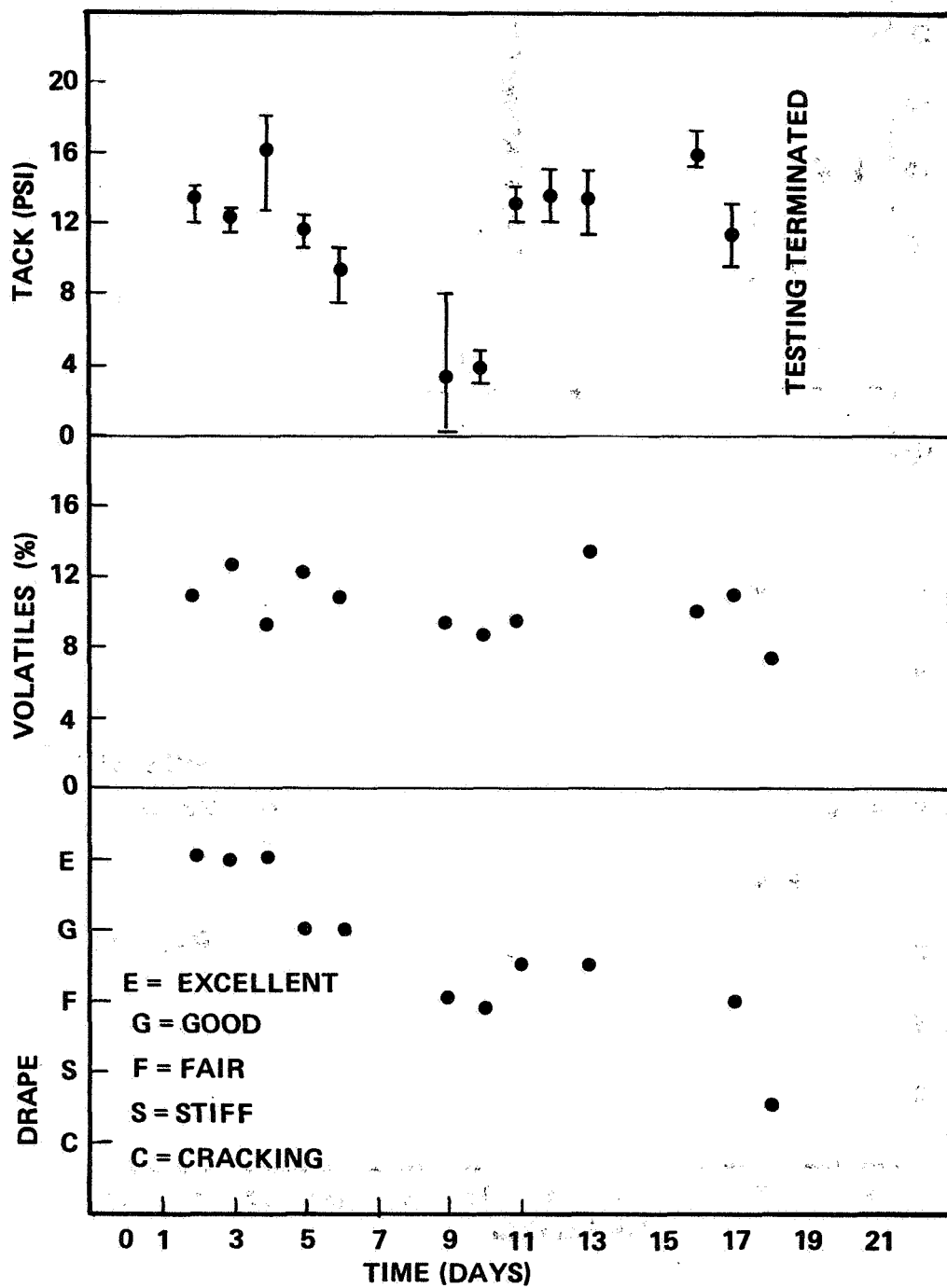
Figure 6: Change in Prepreg Characteristics with Time
Formulation 6: NMA + Diglyme (0.4 moles + 20 w/o)

2.3 BULK RESIN STUDIES

In this study PMR solutions, at a 50% w/w uncured solid level, employing either methanol or ethanol as a carrier solvent and diglyme as a fugative solvent were prepared. These were used to fabricate neat resin specimens which were subjected to thermal mechanical analysis and isothermal gravimetric analysis. This evaluation was used to select two improved tack formulations for composite processing studies. The data from this task have been summarized in Table 4.

Neat resin specimens, 20.6 cm x 20.6 cm x 1.5 cm (8.1 in x 8.1 in x 0.06 in), were fabricated by first imidizing the select solutions to obtain a molding powder and then molding the powder under heat and pressure to obtain the specimens (Reference 3). Imidized powders were obtained by drying the solutions in an air circulating oven at 355°K (180°F) for 72 hours. During drying the beakers containing the solutions were covered to avoid contamination by air borne impurities. The dried materials were then broken into pieces, imidized for two hours at 477°K (400°F) and ground into fine powders using a mortar and pestle.

The imidized powder was put into a cold die, which was then placed into a press between heated platens. About 10% excess molding powder was used to provide resin flash for checking fluidity during molding. Stops were used to prevent complete expulsion of the resin during its viscosity drop. When the extruded flash reached gelation, the stops were withdrawn and pressure reapplied. Each molding was cured for one hour at 588°K (600°F) in the die and then post cured, free standing for 16 hours at 588°K (600°F).

Triplicate specimens, approximately 5 cm x 5 cm x 1.5 mm (21 in x 2 in x 0.06 in), of each of the moldings shown in Table 4 were subjected to isothermal gravimetric analysis at 588°K (600°F). The equipment and procedures used for this are described in Appendix B. A plot of percentage weight loss versus time for these specimens is given in Figure 7.

Thermal mechanical analysis was also performed on sections of these moldings. The glass transition temperatures and coefficients of thermal expansion deduced from the TMA profiles are summarized in Table 4. The procedures used to perform this analysis and estimate the Tg of the

2-15
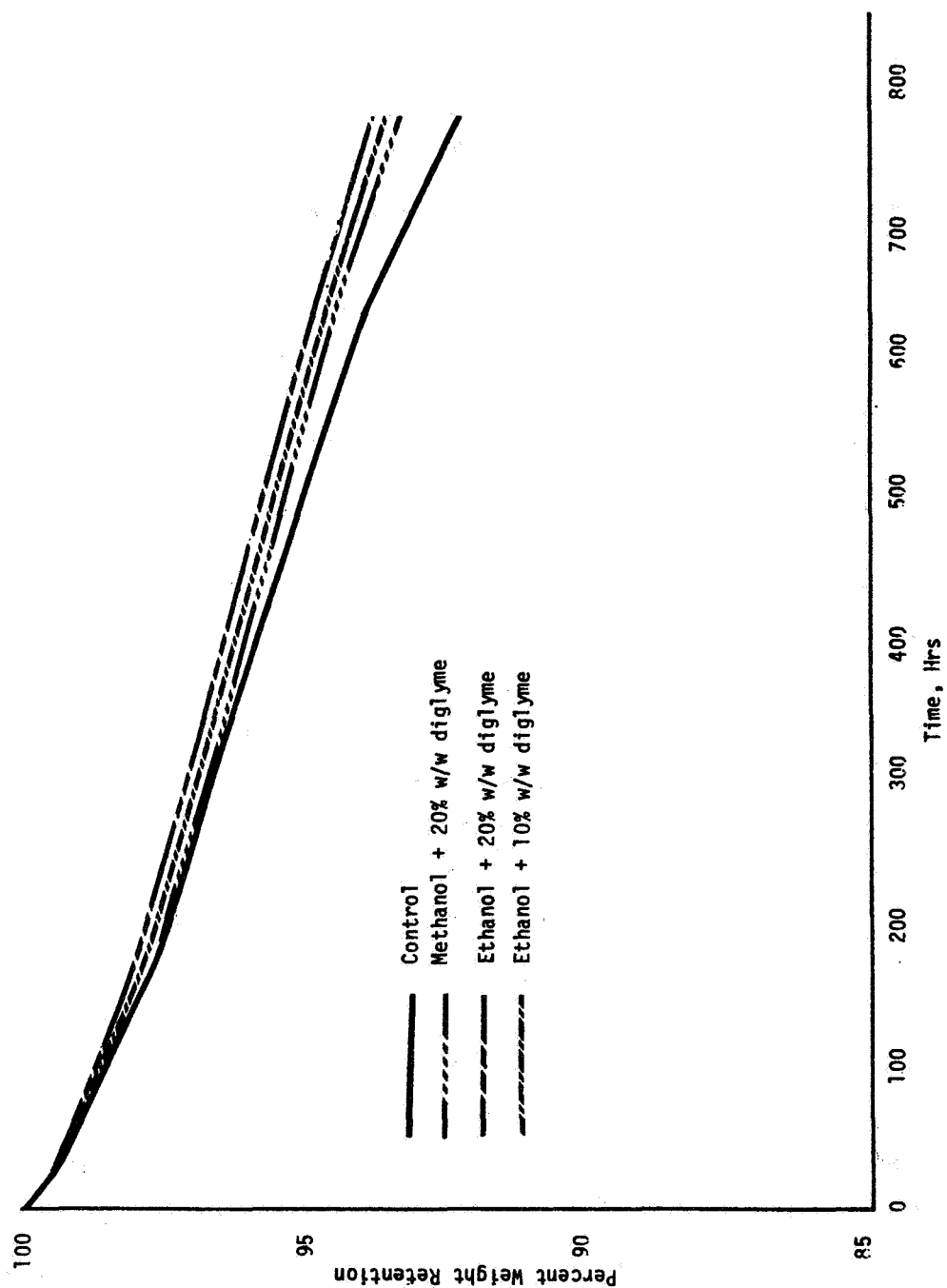
Figure 7. Weight Loss of Neat Resin Moldings of Improved Tack PMR-15 Systems After Isothermal Aging at 588°F (600°F).

Table 4

Thermal Analysis of Improved Tack PMR Neat Resin Moldings

Molding[1]	Solvent System	Figure	Glass Transition Temp., ^{o}K (^{o}F)		Linear Coefficient of Thermal Expansion, $^{o}K^{-1}$, ($^{o}F^{-1}$) $\times 10^{5}$		Weight Loss, 600 Hrs at 588°K (600°F), % w/w
881-38	50% w/w Methanol	C-1	616	(649)	4.4	(2.4)	5.8
936-61	40% w/w Methanol + 10% w/w Diglyme	C-2	618	(653)	4.6	(2.6)	5.3
936-62	40% w/w Ethanol + 10% w/w Diglyme	C-3	615	(648)	4.7	(2.6)	5.1
936-64	45% w/w Ethanol + 5% w/w Diglyme	C-4	614	(646)	4.8	(2.7)	5.3

(1) Samples were dried to a constant weight for 24 hours at 394°K (250°F)

polymer are discussed in Appendix C. In addition all the TMA profiles obtained in this report are included in this Appendix.

On review of the data for the thermal analysis of the improved tack PMR neat resin moldings (Table 4), it was concluded that diglyme had no adverse affect upon the thermal mechanical properties or the thermal oxidative stability of the PMR bulk resin moldings. Because the concentration of diglyme had no effect upon these thermal properties, the formulations containing the higher concentration of diglyme with either methanol or ethanol were selected for further evaluation.

3.0 COMPRESSION MOLDING PROCESS DEVELOPMENT
USING WOVEN PREPREG

In this task C-3000 fabric prepregs were prepared from PMR-15 solutions which utilized either the methanol/diglyme or ethanol/diglyme solvent systems which were discussed in Section 2.3. The tack, drape and volatile content of these prepregs were evaluated both before and after they were aged for thirty days at $278^{o}K$ ($40^{o}F$). Both fresh and aged prepregs were used in composite processing studies to fabricate 10.2 cm x 10.2 cm x 0.23 cm (4.0 in x 4.0 in x 0.09 in) laminates. These studies evaluated the effect of various imidization cycles upon laminate processing and mechanical properties.

Parallel studies were performed on prepreg prepared by hot melt coating tehcniques. PMR resins were formulated which contained 83% w/w uncured resins solids in the fugitive solvent, diglyme. Two formulations were screened, one based upon the dimethyl ester of BTDA and the other upon the diethyl ester. Both of these employed only diglyme as a solvent; no excess alcohol carrier solvent was employed.

In general, all of the laminates molded were high quality, low void materials with excellent mechanical properties. These properties were equivalent to a conventional PMR-15 fabric composite. There were no variations in prepreg processing or laminate properties which could be attributed to either the alcohol solvent employed, methanol or ethanol, or to the fiber impregnation method employed, solution or hot melt.

Gel permeation chromatography (GPC) characterization of BTDE ester, which were prepared by both solution and hot melt methods, was performed. There were no relationships between the chemical composition of these esters, as defined by GPC, and prepreg processability which could be readily identified.

3.1 SOLUTION COATED PREPREG EVALUATION

In this section the method for preparation of solution coated prepreg and the effect of aging of this prepreg at $278^{\circ}K$ ($40^{\circ}F$) are discussed. The effects of various imidization cycles upon processing are given. Laminate evaluation in terms of several physical, mechanical and thermal properties is presented.

3.1.1 PREPREG PREPARATION

The C-3000 fabric was coated with either the improved tack PMR solutions or a PMR-15 control solution according to the procedures given in Section 2.1. Prepreg employing methanol/diglyme was dried in an air circulating oven for two hours at $322^{\circ}K$ ($120^{\circ}F$), and prepreg employing ethanol/diglyme dried two hours at $333^{\circ}K$ ($140^{\circ}F$). This treatment reduced volatile contents to 12% - 14% w/w, which was optimum in terms of handleability. PMR-15 control prepreg was dried for 16 hours at at ambient temperature.

3.1.2 PREPREG AGING

By using the methods discussed in Appendix A the shelf-life of prepreg employed in the processing studies was followed. Prepregs which were aged at $278^{\circ}K$ ($40^{\circ}F$) were stored in sealed polyethylene bags. Aging at room temperature was done by removing the single plies of prepreg from the bags and placing the plies, face up, upon laboratory benches. Problems were encountered during the program in achieving adequate prepreg shelf-life when release paper was used as a backing. Apparently, diffusion of the tackifier through the paper caused the prepreg to become dry prematurely. However, when mylar was used as a backing material the tack lives of all the prepregs remained in the range of 100 Kpa (14.5 psi) or greater for up to twenty-one days. This increased well beyond the goals of the program. Tack retention exceeded the minimum goals of the program (i.e., seven to fourteen days).

In general there appeared to be little difference in the shelf life, i.e. tack and drape, of the two candidate tackifier systems. However, based upon qualitative and subjective observations, after about 14 days all of the prepregs exhibited only minimal tack and drape necessary for complex part fabrication. Even though the quantitative tack values were high (i.e., > 100 Kpa)(14.5 psi) prepreg handleability had become minimal.

3.1.3 LAMINATE PROCESSING

In this study the effect of the imidization cycle, 30 minutes or 60 minutes at 450°K (350°F) or 477°K (400°F), upon laminate mechanical, physical and thermal properties was examined.

Laminates have been fabricated for this study according to the following steps:

(1) Imidize preform in an air circulating oven for 30 or 60 minutes at 450°K (350°F) or 477°K (400°F)

(2) Place the preform in a mold preheated to 505°K (450°F) and apply contact pressure.

(3) Hold at this temperature and pressure for 10 minutes and then apply 3.4 MPa (500 psi) and raise the temperature to 588°K (600°F) at a rate of 4.2°K/min (7.5°F/min.).

(4) Hold at 588°K (600°F) for one hour.

(5) Remove the cloth laminate at 588°K (600°F)

(6) Postcure at 588°K (600°F) for 16 hours

Six plies of prepreg, 10.2 cm (4.0 in.) x 10.2 cm (4.0 in.) were placed between two pieces of porous teflon coated release fabric and two pieces of 181 style E glass for devolatilization and imidization. Caul sheets of thin aluminum were used for support on top and bottom of the preform. Preform pressure was approximately 690 Pa (0.1 psi). A time of temperature profile was plotted using a Hewlett Packard Model 680 strip chart recorder for all preforms and laminates. Temperature

precision was maintained within $\pm$ 1% $^{\circ}$K/$^{\circ}$K, and time precision was maintained within $\pm$ 10% min/min during the imidization and molding processes. Cured laminate thickness was 0.231 cm (0.084 in.) $\pm$ 0.005 cm (0.002 in.).

3.1.4 LAMINATE EVALUATION

The data presented in Tables 5, 6 and 7 are for laminates utilizing methanol (PMR-15 control), methanol/diglyme and ethanol/diglyme solvent systems respectively. The procedures and methods used to measure the physical and mechanical properties reported in these tables are given in Appendix D. These data do not reveal any significant difference in the properties of the laminates which could be attributed solely to a tackifier system. However, there is some evidence that an imidization temperature of at least 477°K (400°F) is necessary for complete de-volatilization of the preforms used in this study.

The data presented in Tables 6 and 7 can be categorized into mechanical, physical and thermal properties to aid in their interpretation. Bar graphs have been constructed which compare the properties of the two tackifiers systems as a function of the imidization cycle. Mechanical properties at 588°K (600°F) are shown in Figure 8 and physical properties of the laminates are shown in Figure 9.

Retention of the tackifier, diglyme, in the cured laminates would have a plasticizing effect upon the PMR matrix at elevated temperature, resulting in a loss of matrix modulus and strength. This would reduce composite mechanical properties, namely flexure and shear strengths at the elevated temperatures. No such trend was seen in this study.

The mechanical properties at 588°K (600°F), which are shown in the bar graph in Figure 8, are all consistently high and compare favorably to the PMR-15 cloth laminate properties shown in Table 5. Variations in strengths obtained with laminates in this study can be attributed to data scatter. There is no identifiable trend in mechanical properties which can be attributed to either variation in imidization cycle or tackifier system.

Table 5. COMPRESSION MOLDING PROCESS STUDY
PMR-15 CONTROL

Imidization Cycle	
Temperature, $^{\circ}$K ($^{\circ}$F)	477 (400)
Time, min.	60
Composite Number	17
Prepreg Properties	
Tackifier	None
Conditioning [1]	Fresh
Resin Content (cured), % w/w	37.88
Volatile Content, % w/w	10.09
Imidized Preform Properties	
Resin Content (cured), % w/w	35.68
Volatile Content, % w/w	10.02
Extent of Volatile Expulsion, % w/w	99
Composite Properties	
Flexural Strength, MPa (Ksi)	
R.T.	1010 (146)
588°K (600°F)	800 (116)
Flexural Modulus, GPa (Msi)	
R.T.	58 (8.4)
588°K (600°F)	57 (8.3)
Shear Strength MPa (Ksi)	
R.T.	58 (8.4)
588°K (600°F)	46 (6.7)
Appearance After Molding [2]	E
Flow, % w/w	0.9
Density, g/cc	1.562
Resin Content, % w/w	35.28
Fiber Volume, % v/v	57.44
Void Volume, % v/v	0.8

(1) Fresh prepreg was stored at 243°K (-22°F) for a maximum of 10 days.

(2) E (excellent), uniform smooth and free of surface defects.
   G (good), some surface discoloration near the periphery of the laminate, no visually detectable porosity
   F (fair), general surface discoloration and slight porosity near the periphery of the laminate
   P (poor), general surface depressions and porosity

Table 6. COMPRESSION MOLDING PROCESS STUDY
METHANOL/DIGLYME SOLVENT SYSTEM (80/20 p.b.w.)

						457 (410) 80		
Imidization Cycle								
Temperature, °K (°F)	655 (380)	464 (360)	477 (400)	464 (360)	477 (410)			
Time, min.	90	60	90	60	80			
Composite Number	6	7	2	7	9		11	15
Prepreg Properties								
Conditioning (1)	Fresh	Fresh	Fresh	Fresh	Fresh		Aged	Aged
Resin Content (cured), % w/w	38.5	38.6	40.6	40.5	37.9		38.4	34.4
Volatile Content, % w/w	12.6	13.8	15.2	15.2	13.2		12.7	10.8
Imidized Preform Properties								
Resin Content (cured), % w/w	37.7	32.8	32.3	38.9	32.8		37.8	38.7
Volatile Content, % w/w	12.3	12.8	14.5	14.5	13.1		12.1	11.0
Extent of Volatile Expulsion, % w/w (2)	90	94	96	98	98		96	96
Composite Properties								
Flexural Strength, MPa (ksi)								
R.T.	924 (134)	966 (139)	1027 (149)	1007 (146)	1068 (155)		966 (143)	1048 (152)
589°K (600°F)	607 (88)	662 (96)	676 (98)	834 (88)	731 (106)		824 (92)	752 (109)
Flexural Modulus, GPa (Msi)								
R.T.	57 (8.2)	59 (8.5)	61 (6.8)	59 (8.6)	75 (10.9)		68 (9.8)	69 (9.2)
589°K (600°F)	51 (7.4)	57 (8.2)	53 (7.7)	62 (7.6)	70 (10.2)		54 (8.1)	65 (9.4)
Shear Strength MPa (ksi)								
R.T.	64 (9.3)	68 (9.9)	63 (9.2)	65 (9.5)	59 (8.4)		62 (9.0)	66 (9.6)
589°K (600°F)	45 (6.5)	49 (7.1)	42 (6.1)	41 (6.4)	38 (5.5)		38 (5.5)	47 (6.4)
TMA Flaws No.	C–6	C–7	C–8	C–9	C–10		C–11	E
Glass Transition Temperature, °K (°F)	536 (505)	562 (554)	550 (531)	465 (558)	535 (504)		537 (507)	72
Appearance After Molding (2)	G	G	F	E	E		E	1.574
Flow, % w/w	3.8	1.9	1.8	1.2	1.0		2.2	32.77
Density, g/cc	1.556	1.568	1.586	1.586	1.574		1.563	63.19
Resin Content, % w/w	37.08	36.90	37.64	38.73	33.19		36.81	0.8
Fiber Volume, % v/v	65.77	65.79	55.17	63.30	63.95		63.76	
Void Volume, % v/v	4.6	0.7	2.5	0.9	0.7		0.9	

(1) Fresh prepreg was stored at 244°K (-22°F) for a maximum of 10 days.
Aged prepreg was stored at 297°K (75°F) for 30 days and then at
ambient conditions for 7 days (laminate 11) or 14 days (laminate 15).

(2) E (excellent); uniform, smooth and free of surface defects.
G (good); some surface discoloration near the periphery of the
laminate, no visually detectable porosity
F (fair); present surface discoloration and slight porosity near
the periphery of the laminate
P (poor); general surface degradation and porosity

Table 7. COMPRESSION MOLDING PROCESS STUDY ETHANOL/DIGLYME SOLVENT SYSTEM (80/20 p.b.w.)

					477 (400)		
Imidization Cycle							
Temperature, °K (°F)	450 (350)	450 (350)	477 (400)				
Time, min.	30	60	30		60		
Composite Number	8	5	4	3	10	12	16
Prepreg Properties							
Conditioning (1)	Fresh	Fresh	Fresh	Fresh	Fresh	Aged	Aged
Resin Content (cured), % w/w	38.6	40.0	40.0	40.0	33.6	38.6	35.6
Volatile Content, % w/w	13.2	17.4	17.4	17.4	14.9	12.5	12.1
Imidized Preform Properties							
Resin Content (cured), % w/w	37.5	36.0	35.4	35.3	-	37.5	34.5
Volatile Content, % w/w	12.4	16.3	16.9	16.8	-	11.9	11.3
Extent of Volatile Expulsion, % w/w (2)	94	94	97	97	-	95	94
Composite Properties							
Flexural Strength, MPa (ksi)							
R.T.	1041 (151)	1076 (156)	869 (129)	958 (139)	1145 (166)	1014 (147)	979 (142)
588°K (600°F)	689 (100)	683 (99)	648 (94)	648 (94)	841 (122)	662 (96)	717 (104)
Flexural Modulus, GPa (Msi)							
R.T.	61 (8.9)	64 (9.3)	57 (8.3)	56 (8.1)	73 (10.6)	60 (8.7)	62 (9.0)
588°K (600°F)	58 (8.4)	59 (8.5)	54 (7.9)	52 (7.5)	76 (11.0)	57 (8.3)	61 (8.8)
Shear Strength MPa (ksi)							
R.T.	57 (8.3)	61 (8.9)	66 (9.6)	64 (9.3)	56 (8.1)	56 (8.1)	70 (10.2)
588°K (600°F)	44 (6.4)	45 (6.5)	44 (6.4)	43 (6.3)	41 (6.0)	37 (5.4)	43 (6.3)
TMA Figure No.	C-12	C-13	C-14	C-15	C-16	C-17	
Glass Transition Temperature, °K (°F)	545 (522)	566 (559)	582 (588)	549 (529)	546 (523)	544 (520)	
Appearance After Molding (2)	E	E	E	E	G	E	E
Flow, % w/w	2.6	2.4	1.3	1.1	1.0	0.9	0.9
Density, g/cc	1.557	1.573	1.571	1.563	1.568	1.558	1.561
Resin Content, % w/w	36.60	34.07	34.48	35.15	37.8	37.34	33.19
Fiber Volume, % v/v	56.09	58.93	58.49	57.60	60.75	55.47	59.26
Void Volume, % v/v	0.8	0.5	0.5	0.8	1.4	0.5	1.4

1) Fresh prepreg was stored at 243°K (-22°F) for a maximum of 10 days. Aged prepreg was stored at 278°K (40°F) for 30 days and then at ambient conditions for 7 days (laminate 12) or 14 days (laminate 16).

(2) E (excellent), uniform, smooth and free of surface defects.

    G (good), some surface discoloration near the periphery of the laminate, no visually detectable porosity

    F (fair), general surface discoloration and slight porosity near the periphery of the laminate
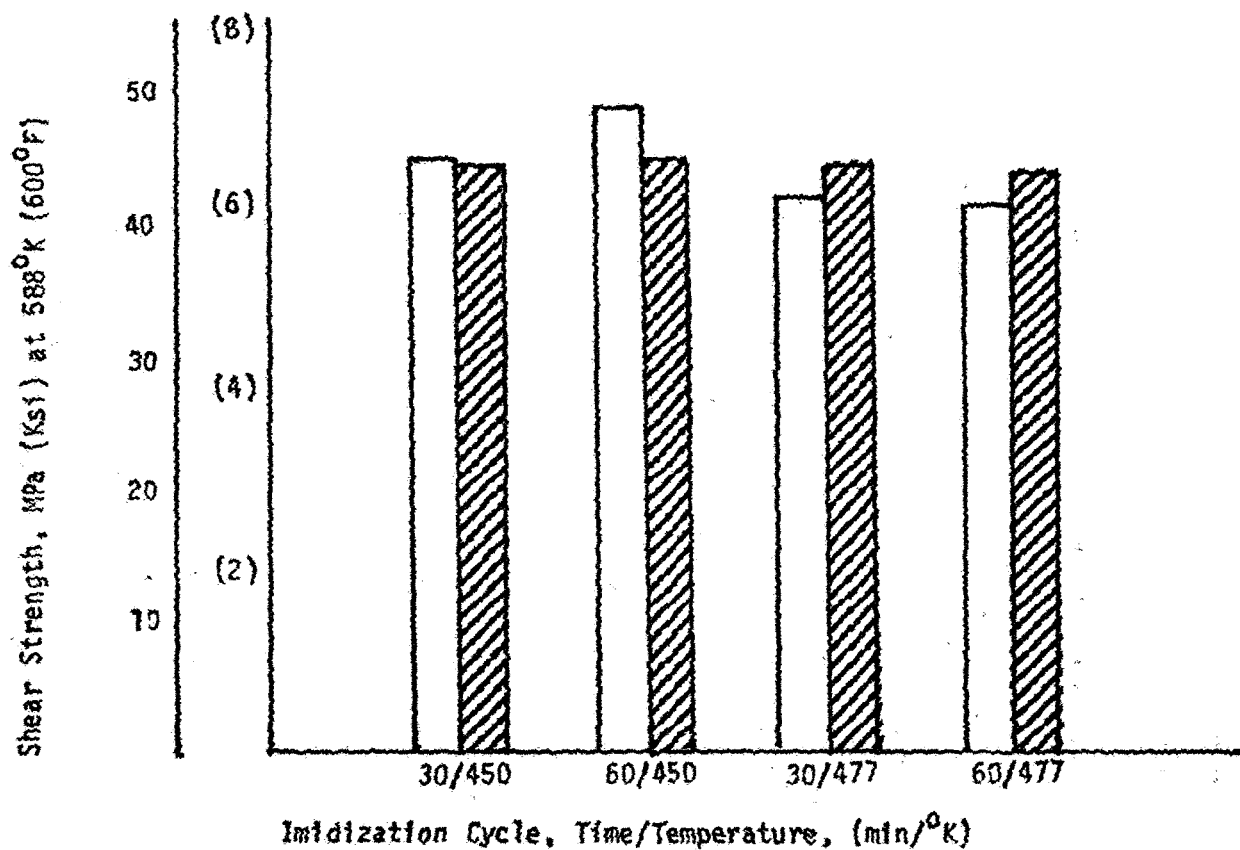
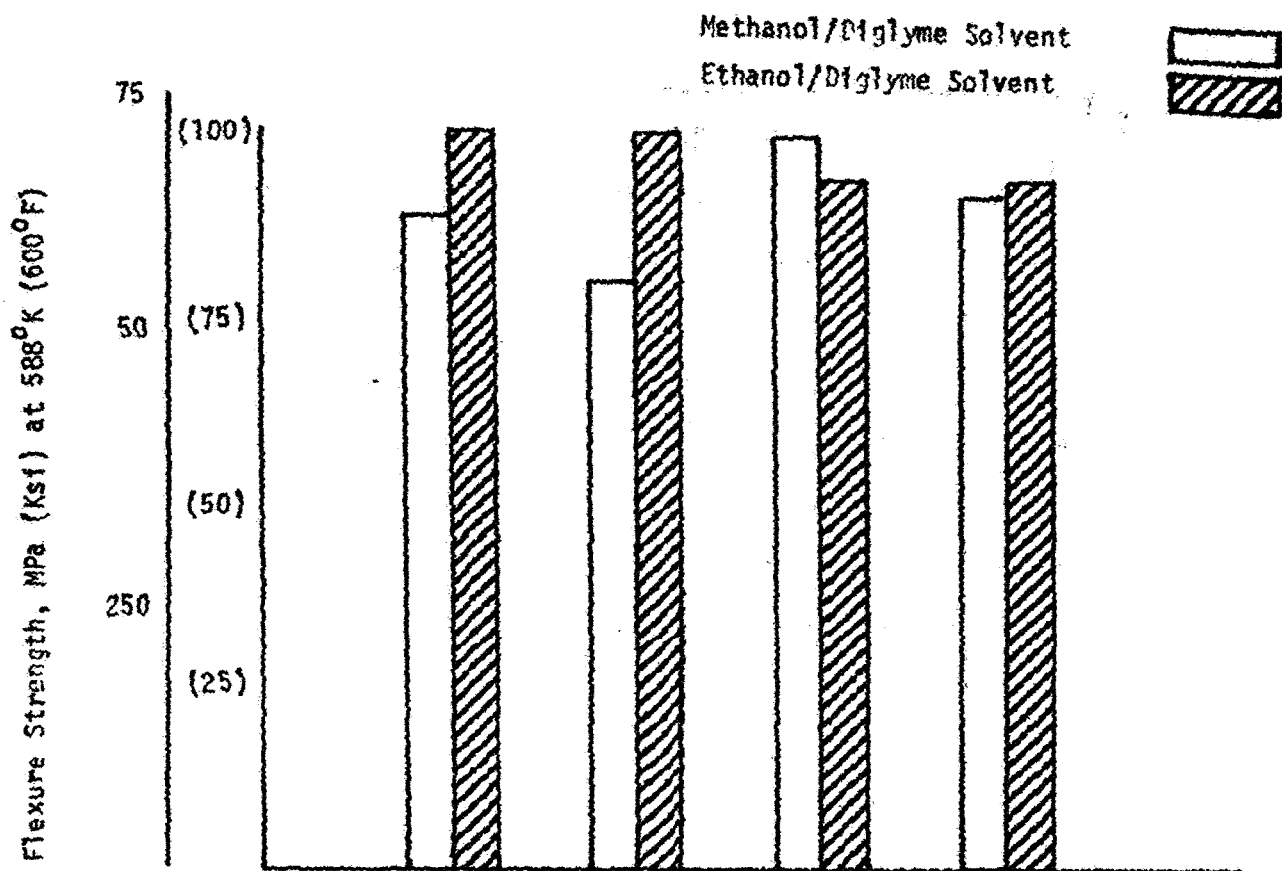   P (poor), general surface depressions and porosity

FIGURE 8. Laminate Mechanical Properties versus Imidization Cycle
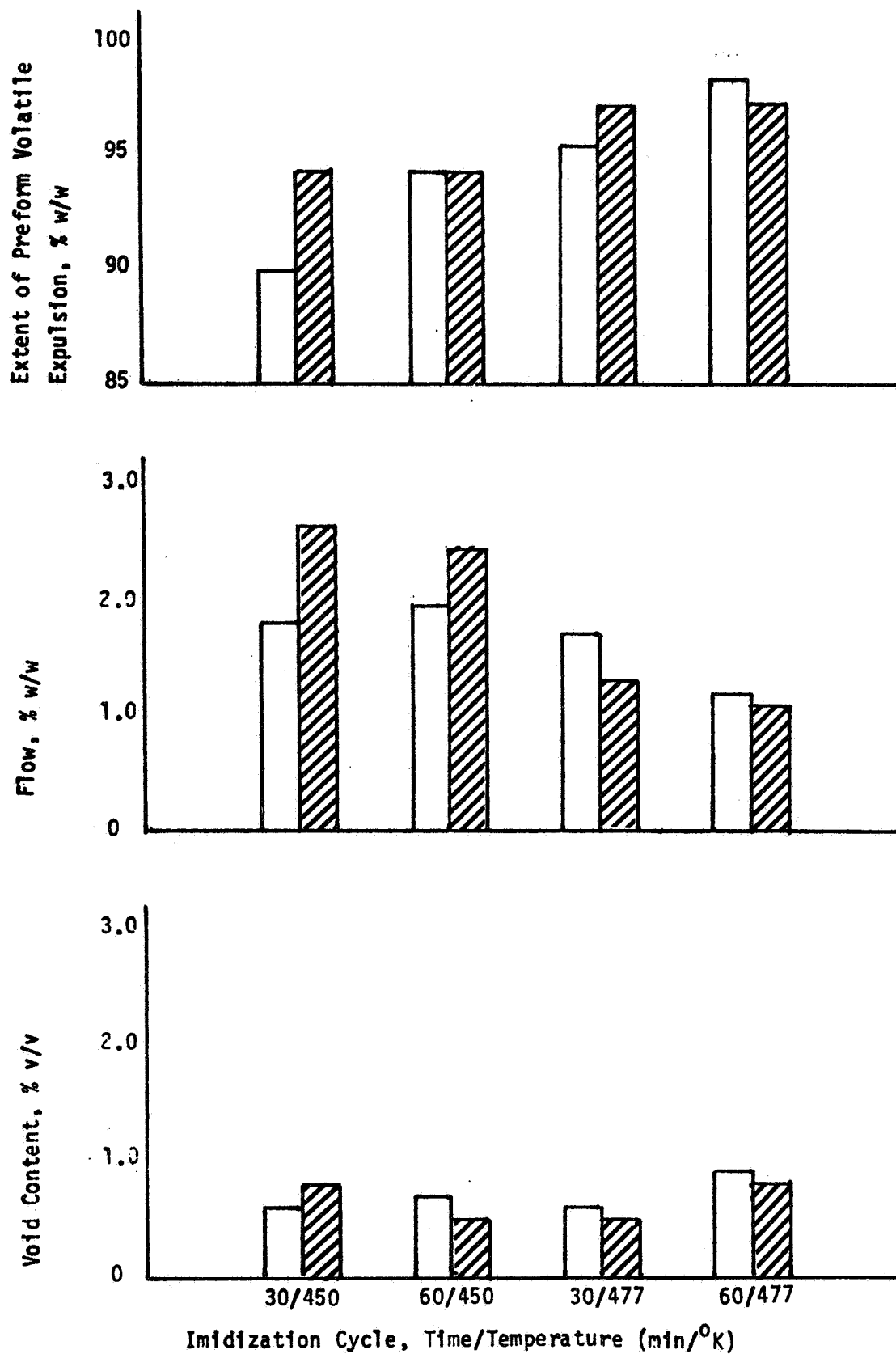
FIGURE 9. Laminate Physical Properties versus Imidization Cycle

Methanol Diglyme Solvent

Ethanol Diglyme Solvent

To get an indication of any residual solvents or condensation products in the laminate preforms after the imidization cycles, the volatile contents of the preforms were determined. These were determined by gravimetric methods given in Appendix E. Complete devolatilization of a preform should provide a value for its volatile content that is identical to the prepreg volatile content. Preform volatile contents that are less than the prepreg volatile would indicate only partial devolatilization. Division of the preform volatile content by the prepreg volatile content would thus indicate the efficiency of the imidization cycle, with 100% being an optimum value. As can be seen in Figure 9, milder imidization cycles at $450^\circ K$ ($350^\circ F$) did not completely remove all of the volatile matter from the preforms, while essentially all was removed with a $477^\circ K$ ($400^\circ F$) cycle.

Two additional physical properties which are shown in Figure 13 are resin flow during molding and laminate void content. The flow data are highly subjective, i.e., they are dependent upon the type of reinforcement, mold geometry etc.. However, the data in Figure 9 can be used for comparison purposes; they indicate that higher imidization temperatures reduce resin flow during molding. This is consistent with previous work with the PMR-15 system (Reference 2). Higher imidization temperatures, $505^\circ K$ ($450^\circ F$), would possibly reduce flow during molding to a point where complete matrix consolidation would not take place. The void contents of these laminates were determined on six shear test specimens, which were taken from random locations on each laminate. The data shown in Figure 9 are all indicative of essentially void free, high quality laminates. Variation of imidization cycle or tackifier did not have an effect upon laminate void content. Preforms imidized at $450^\circ K$ ($350^\circ F$) were determined to contain significant residual volatile matter. It might be anticipated that higher void content laminates would result from these preforms, however, this was not observed. An explanation for this could be that substantial volatile matter was released in the mold during the ten minute dwell at $505^\circ K$ ($450^\circ F$) under contact pressure.

Thermal mechanical analysis (TMA) was conducted on most of the laminates fabricated in this study. Tha apparent transition temperatures of the laminates are given in Tables 5 through 7. A representative TMA profile is given in Appendix C. With all laminates, both improved tack PMR and PMR-15 control there was an increase in the expansion rate of all of these laminates between $543^\circ K$ ($518^\circ F$) and $588^\circ K$ ($600^\circ F$). This indicates that the apparent glass transition temperatures of the laminates are in this range and are $28^\circ K$ ($50^\circ F$) to $56^\circ K$ ($100^\circ F$) less than the glass transition temperatures found for the analogous neat resin samples (Table 4). This anomaly was perplexing because the mechanical properties of the laminates at $588^\circ K$ ($600^\circ F$) were indicative of a material still below its T_g. That is, flexure and shear specimens failed in a brittle mode, which was indicative of a cured matrix possessing relatively high modulus. The TMA instrumentation and experimental technique was critically reviewed to see if the expansion curves might be erroneous. No discrepancy could be found, so the transitions interpreted from the TMA profiles were considered realistic.

A possible explanation for this discrepancy could be matrix failure on a micromechanical scale caused by induced thermal stresses. In $0^\circ-90^\circ$, i.e., fabric, laminates relatively high matrix compressive stresses exist in the fiber directions due to the negative coefficient of expansion of the reinforcement. This will cause high matrix tensile stresses to be induced in the direction perpendicular to the plane of the laminate because of a poisson's ratio effect. In areas of high stress concentration local matrix failure could occur; the remaining intact matrix would naturally have to experience a higher strain to maintain the same average induced stress in the direction perpendicular to the plane of the laminate. Conceivably the induced thermal stresses could be high enough at temperatures below the true matrix T_g, so that microstructural matrix fracture could occur. The resultant laminate strain increase would mask any real increase in the rate of expansion of the matrix.

If this concept is valid there should be a higher coefficient expansion seen in fabric laminates than in unidirectional laminates. This would be expected since compressive matrix stresses are present in two directions in fabric laminates but are present only in one direction in unidirectional laminates. The coefficients of thermal expansion, in this direction, for the PMR-15 control fabric and unidirectional laminates were 5.23 x 10^{-5} $^{o}C^{-1}$ and 3.44 x 10^{-5} $^{o}C^{-1}$ respectively. This is a significant difference in expansion coefficients, which might imply that induced thermal strains were masking the actual T_g's of the matrix in the fabric composites.

The isothermal gravimetric analysis of the laminates fabricated in the compression molding process study, numbers 1 through 16, was conducted using the procedures and apparatus described in Appendix B. Weight losses of triplicate specimens, 5.1 cm x 1.3 cm x 0.23 cm (2.0 in. x 0.5 in. x 0.09 in.), from each laminate were monitored. Weight loss data for these laminates, which were exposed to 588°K (600°F) are summarized in Figures 10 through 13. The data for laminates which were imidized at various times and temperatures are presented in Figures 10 and 11. Figures 12 and 13 present data for laminates which were processed identically, using fresh and aged prepreg, and thus give an indication of reproducibility.

All of these data are similar to that reported for conventional PMR-15/C-3000 cloth laminates (Reference 3). Apparently, the use of the tackifier, diglyme, has not had a grossly deleterious effect upon the thermogravemetric behavior of these cloth laminates. However, in an attempt to define any possible effects of the imidization cycle and possible residual diglyme upon thermal stability, the data in Figures 10 and 11 have been further reduced in Figure 14. This bar graph shows how the weight loss, after 600 hours exposure at 588°K (600°F), of the cloth laminates varies with increasing degrees of imidization. These data have been normalized in terms of resin content to provide more meaningful comparison. Weight loss data at elevated temperatures are certainly a function of many factors and generally exhibit high variability. The data in Figure 14 do vary. However, there appears to be trend to less
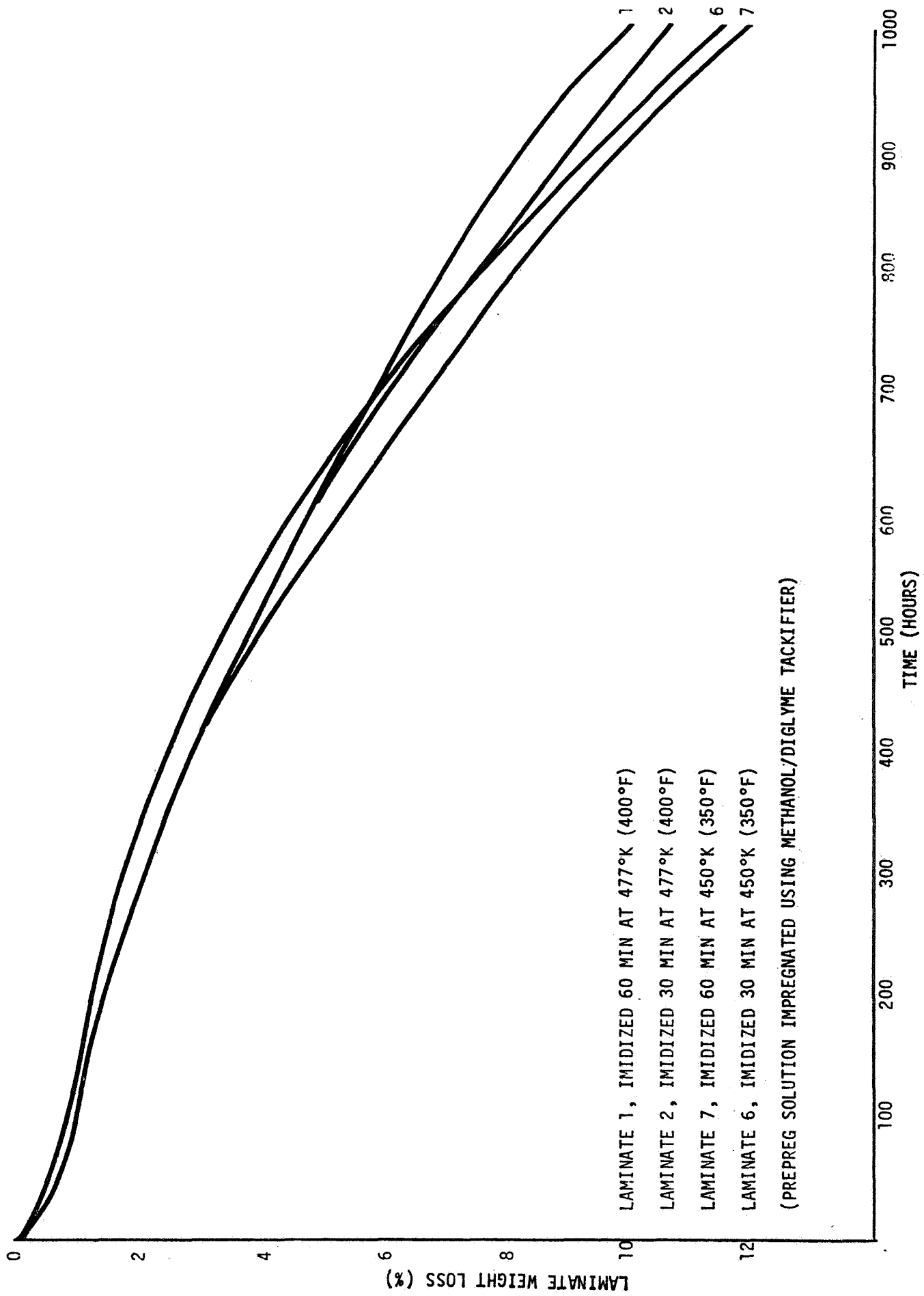
FIGURE 10. WEIGHT LOSS OF IMPROVED TACK PMR/C-3000 CLOTH LAMINATES EXPOSED TO 589°K (600°F)

LAMINATE 1, IMIDIZED 60 MIN AT 477°K (400°F)

LAMINATE 2, IMIDIZED 30 MIN AT 477°K (400°F)

LAMINATE 7, IMIDIZED 60 MIN AT 450°K (350°F)

LAMINATE 6, IMIDIZED 30 MIN AT 450°K (350°F)

(PREPREG SOLUTION IMPREGNATED USING METHANOL/DIGLYME TACKIFIER)
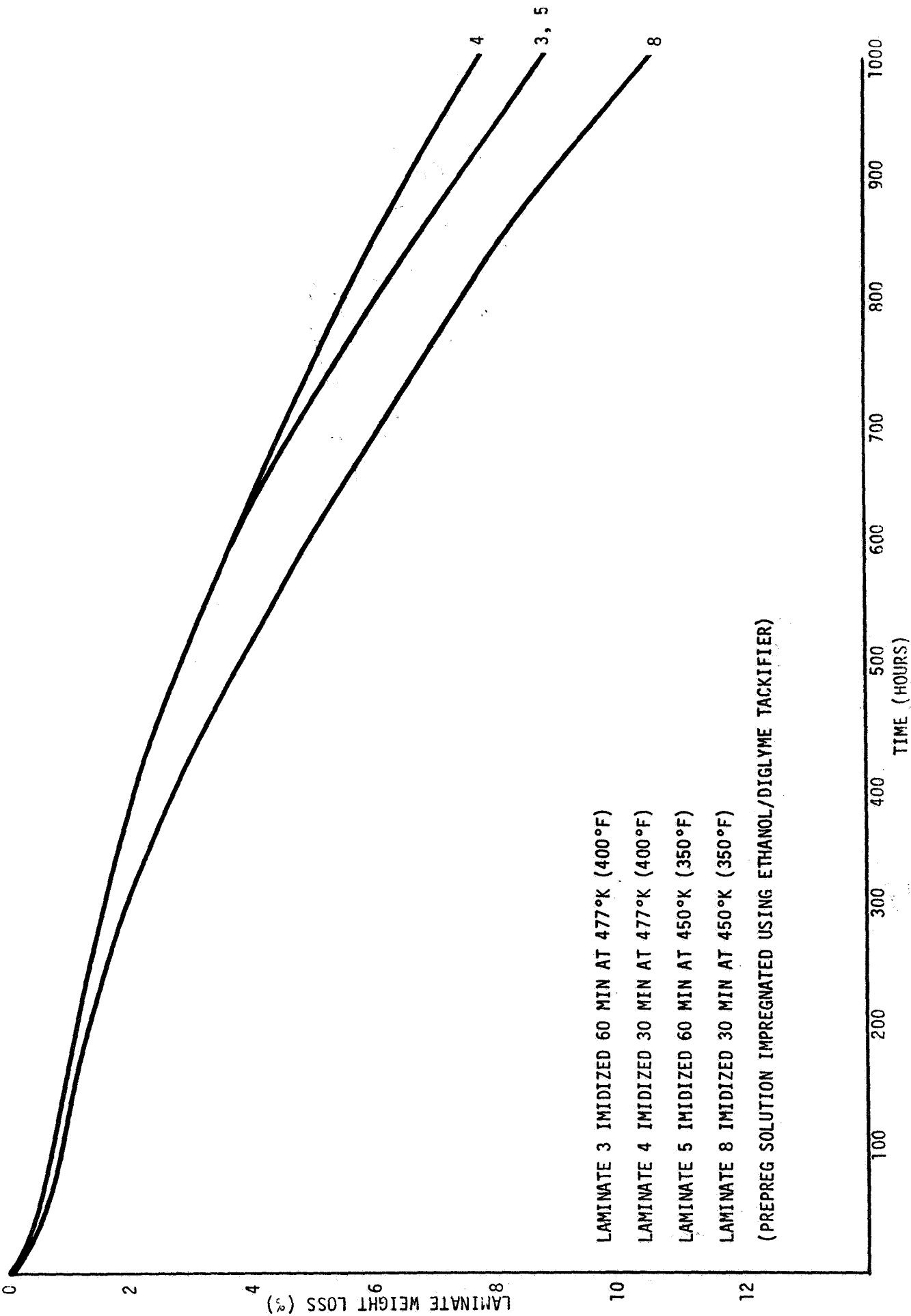
FIGURE 11. WEIGHT LOSS OF IMPROVED TACK PMR/C-3000 CLOTH
LAMINATES EXPOSED TO 589°K (600°F)

LAMINATE 3 IMIDIZED 60 MIN AT 477°K (400°F)
LAMINATE 4 IMIDIZED 30 MIN AT 477°K (400°F)
LAMINATE 5 IMIDIZED 60 MIN AT 450°K (350°F)
LAMINATE 8 IMIDIZED 30 MIN AT 450°K (350°F)
(PREPREG SOLUTION IMPREGNATED USING ETHANOL/DIGLYME TACKIFIER)
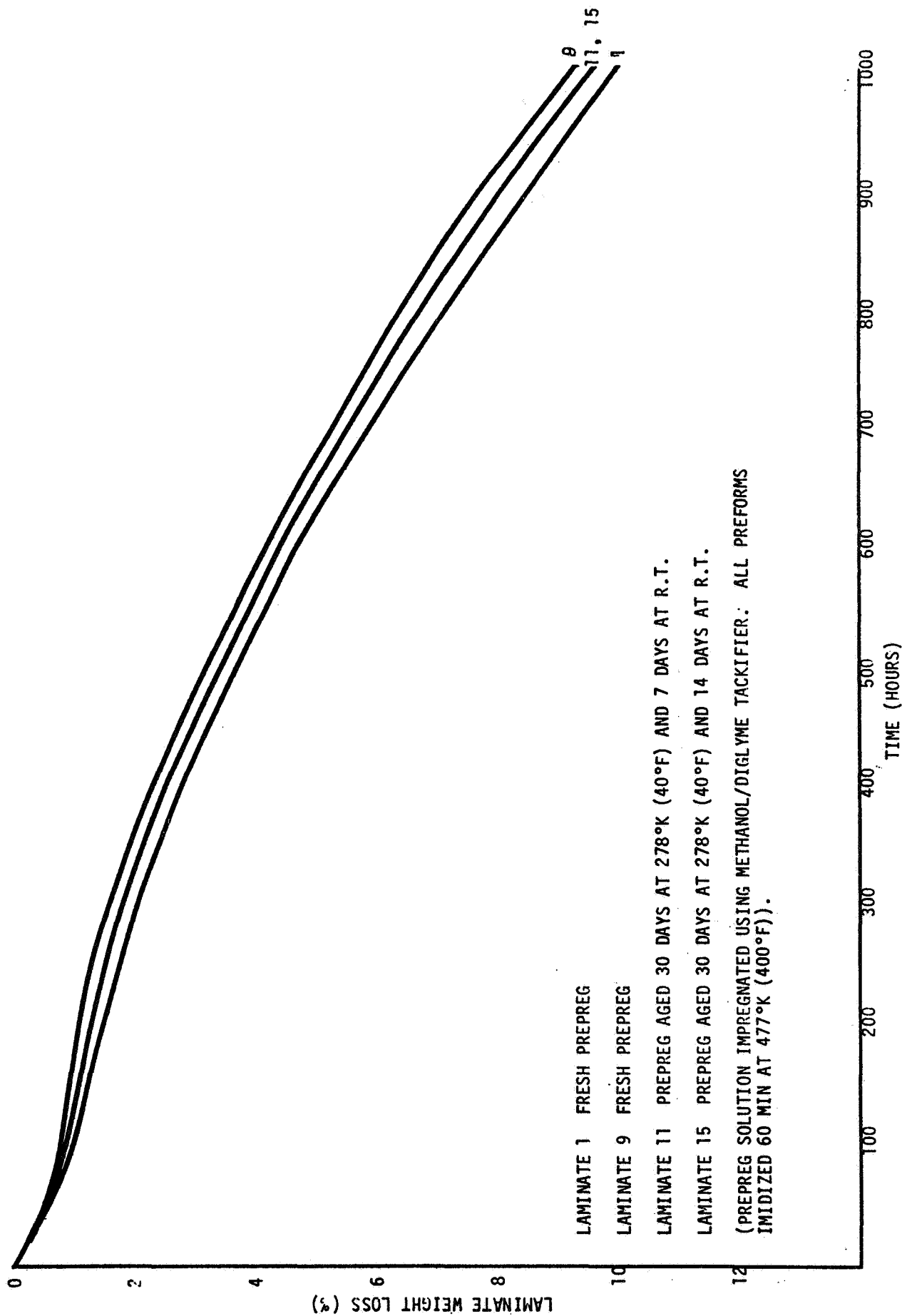
FIGURE 12 WEIGHT LOSS OF IMPROVED TACK PMR/C-3000 CLOTH LAMINATES EXPOSED TO 589°K (600°F)

LAMINATE 1   FRESH PREPREG

LAMINATE 9   FRESH PREPREG

LAMINATE 11   PREPREG AGED 30 DAYS AT 278°K (40°F) AND 7 DAYS AT R.T.

LAMINATE 15   PREPREG AGED 30 DAYS AT 278°K (40°F) AND 14 DAYS AT R.T.

(PREPREG SOLUTION IMPREGNATED USING METHANOL/DIGLYME TACKIFIER: ALL PREFORMS IMIDIZED 60 MIN AT 477°K (400°F)).
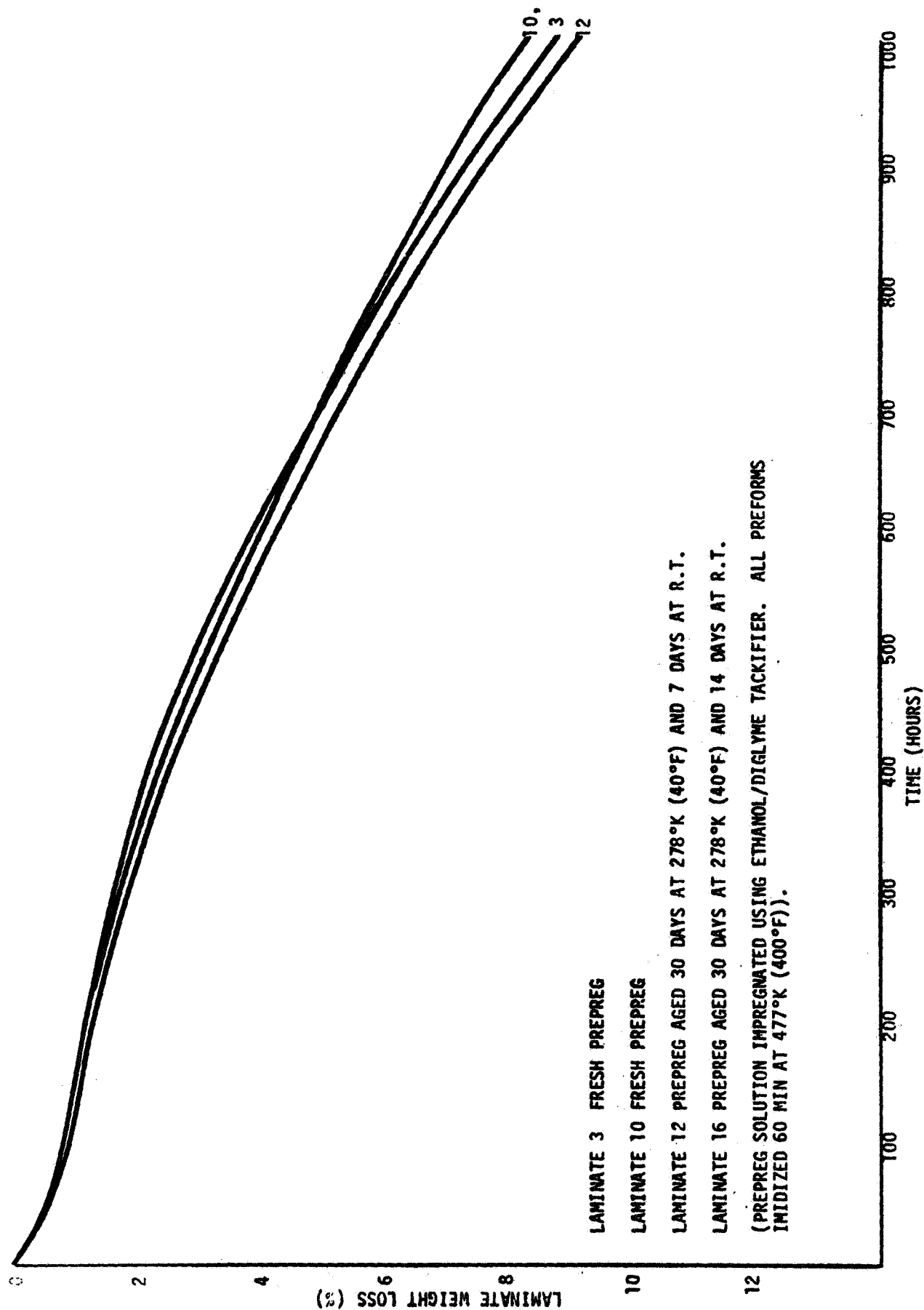
FIGURE 13. WEIGHT LOSS OF IMPROVED TACK PMR/C-3000 CLOTH LAMINATES EXPOSED TO 589°K (600°F)

LAMINATE 3   FRESH PREPREG

LAMINATE 10 FRESH PREPREG

LAMINATE 12 PREPREG AGED 30 DAYS AT 278°K (40°F) AND 7 DAYS AT R.T.

LAMINATE 16 PREPREG AGED 30 DAYS AT 278°K (40°F) AND 14 DAYS AT R.T.

(PREPREG SOLUTION IMPREGNATED USING ETHANOL/DIGLYME TACKIFIER. ALL PREFORMS IMIDIZED 60 MIN AT 477°K (400°F)).
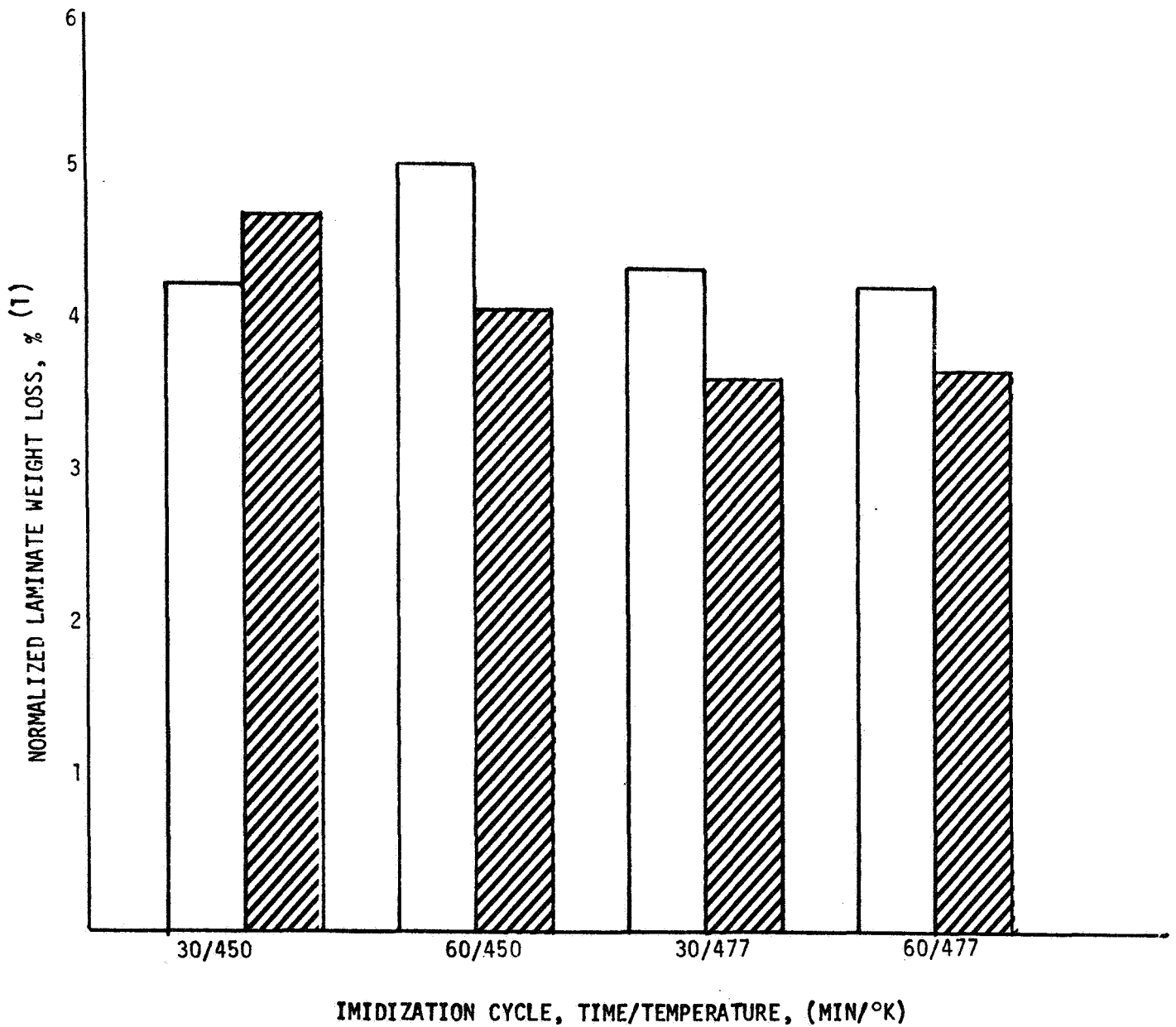
FIGURE 14. LAMINATE WEIGHT LOSS AFTER 600 HOURS EXPOSURE TO 589°K (600°F)

METHANOL/DIGLYME SOLVENT

ETHANOL/DIGLYME SOLVENT

(1) WEIGHT LOSSES ARE NORMALIZED TO A LAMINATE RESIN CONTENT OF 34%:

$$\text{NORMALIZED WEIGHT LOSS (\%)} = \text{MEASURED WEIGHT LOSS} \times \left(\frac{.3400}{\text{LAMINATE RESIN CONTENT}} \right)$$

weight loss with greater degrees of imidization. This probably is a realistic trend.

In summary, the mechanical properties of all the laminates evaluated in this section were comparable to those of a PMR-15 control laminate. In addition these properties were independent of the imidization cycles or tackifiers which were studied. The laminate physical properties were somewhat dependent upon the imidization cycle. For optimum devolatilization of the preform, adequate resin flow during molding and low laminate void content an imidization cycle of one hour at 477°K (400°F) appeared necessary. In addition there was slight evidence that imidization at 477°K (400°F) produced laminates of higher thermoxidative stability. TMA analysis of fabric laminates produced values for matrix glass transition temperatures which were abnormally low. This could be attributable to matrix failure on a micromechanical scale due to induced thermal stresses.

3.2 HOT MELT COATED PREPREG EVALUATION

In this section the preparation of hot melt processable improved tack PMR resins and prepregs is discussed. The effects of aging upon tack lives of these materials is given. Prepreg processing and laminate evaluation of these materials are summarized and compared to the results found for solution impregnated prepregs.

3.2.1 HOT MELT RESIN PREPARATION

Hot melt, versions of the improved tack PMR system, based on the dimethyl/or diethyl ester of BTDA, were prepared by using the ratio of ingredients shown for formulation 2. However, the excess amounts of either methanol or ethanol used for carrier solvent purposes were eliminated. In this procedure the tackifier, diglyme, was used as the solvent for the esterification of the BTDA. Each mole of BTDA was esterified with equivalent amounts (two moles) of either methanol or ethanol.

A resin kettle equipped with an efficient stirring paddle, heating mantle, thermocouple with strip chart recorder, and reflux condenser was employed for the preparation of all of the hot melt formulations. Esterification was performed by mixing the BTDA, appropriate alcohol and diglyme at room temperature. This was slowly heated at 1^{O}K/min (2^{O}F/min); between 353°K and 363°K (175°F and 195°F) the slurry transformed into a clear solution. The solution was heated an additional 15 minutes at 373°K (212°F) and then cooled. This resultant solution had a diester concentration of 69% w/w. Upon cooling to 339°K (150°F) the remaining NE and MDA solids were added. All ingredients dissolved within 5 minutes. This mixture was degassed by using an aspirator vacuum source for 5 minutes. The uncured resin solids concentration of these formulations was 83.3% w/w. The consistency of these resins appeared ideal for hot melt processing. Both were semi-solid at ambient temperatures, and both thinned to light syrup consistency (1,000 cps - 10,000 cps) at 328°K (130°F).

To verify that a high conversion of the dianhydride to diester had taken place, chemical analysis for residual anhydride was performed on the high solids BTDE products. The results of this volumetric and infrared spectral analysis are given in Table 8. The titration method is summarized on the table, and a detailed procedure is referenced (Ref. 4). The volumetric analysis of the BTDA, the BTDE methyl ester and the BTDE ethyl ester indicate that about 95% of the anhydride groups have been esterified. Similar

A confirmation of this conversion was obtained by infrared analysis. These results indicate that esterification, by this hot melt technique, was nearly quantitative. The composition of these BTDE ester products should be essentially diester and thus nearly identical to the BTDE obtained by the conventional technique of refluxing BTDA in a 50% w/w solution in alcohol. However, since the hot melt versions of BTDE contain very little residual alcohol, the inherent problems of tri and tetraester formation of BTDE solutions over long periods should be avoided (Reference 5).

TABLE 8   QUANTITATIVE ANALYSIS OF BTDE ESTERS
PREPARED BY HOT MELT TECHNIQUES (1)

Monomer	Total Acid Conc., meq/g	Anhydride Conc., meq/g	Anhydride Content, %	Acid Content, %	I.R. Spectra	
					Fig. No.	Anhydride Band (5.4 m)
BTDA (anhydride)	12.80	5.95	92.7	7.3	5	Strong
BTDE (methylester)	5.61	0.32	5.7	94.3	6	Very weak
BTDE (ethylester)	5.16	0.11	2.1	97.9	7	Very weak

(1) Volumetric analysis according to the procedure given by C. W. Hammond (Reference 4). This involved titration of total acid in water and titration of acid following esterification of the anhydride with methanol. Pyridine was employed as a catalyst in both cases. Acid content was determined with aqueous NaOH.

The GPC analysis of BTDE solutions, 69% w/w in diglyme and 50% w/w in methanol, which were aged at ambient temperatures for up to three months, is discussed in Section 3.3.

3.2.2 HOT MELT PREPREG PREPARATION

Prepreg was prepared using the Celion-3000 woven fabric described in Section 2.2.

Prepreg manufacture involved casting a thin film of resin and then pressing the resin film through the fabric. The film was prepared by pouring a preweighed, warm, 322^OK (120^OF), amount of resin upon a sheet of mylar. This was placed upon a hot plate heated to 333^OK (140^OF). A Gardner Knife was used to cast the film in a uniform thickness. Upon pulling the sheet of mylar and resin beneath the knife edge, it was possible to obtain resin films reproducible to $\pm$ 10% in thickness. Exposure of the thin film 0.020 cm (0.008 inch) to the elevated temperature was kept less than 30 seconds to avoid possible loss of the tackifier. In this experimentation, calculated volatile contents of the hot melt prepregs and experimentally determined volatile contents were identical within experimental error. Thus, it was determined that very little tackifier was lost during the film casting step. Impregnation of the fabric was completed by placing the cloth upon the film and placing a second sheet of mylar upon the cloth. This sandwich was placed in a press preheated to 333^OK (140^OF), and with the aid of a silicone rubber pressure pad the resin film was squuezed through the fibers. The time and pressure required for this step were one minute and 20 Kpa (3 psi) respectively. Upon removal of the top mylar sheet the prepregs appeared to be completely wetted by resin, uniform in quality and quite tacky.

3.2.3 LAMINATE AGING

Tests conducted to determine the tack lives of these prepregs in the manner described in Section 3.1.2 where solution coated materials were evaluated showed that an acceptable level of tack remained in each of the candidate hot melt prepregs for a period of ten to fourteen days and thus exhibited essentially the same tack characteristics as the solution coated prepregs.

3.2.4 LAMINATE PROCESSING

This task was intended to demonstrate that the hot melt versions of the improved tack PMR prepregs could be processing in a manner identical to the solution coated improved tack PMR prepregs. The most promising cycle defined in Section 3.1.3 was used to fabricate these laminates.

3.2.5 LAMINATE EVALUATION

The results are shown in Table 9 for laminates fabricated from hot melt coated prepreg. Inspection of the properties given in this table shows that alteration of the tackifier system did not adversely affect the quality of the laminates. In addition, the properties of these laminates were equivalent to those laminates prepared from solution impregnated fabric. The results of the isothermal gravimetric analysis of sections of these laminates are shown in Figure 15. The weight losses of these laminates upon exposure to $588^{\circ}K$ ($600^{\circ}F$) were comparable to those found for laminates molded from solution coated prepreg.

Table 9. COMPRESSION MOLDING PROCESS STUDY HOT MELT SYSTEMS

Imidization Cycle		
Temperature, $^\circ$K ($^\circ$F)	477 (400)	477 (400)
Time, min.	60	60
Composite Number	13	14
Prepreg Properties		
Tackifier	Methanol/Diglyme	Ethanol/Diglyme
Conditioning [1]	Fresh	Fresh
Resin Content (cured), % w/w	33.3	33.3
Volatile Content, % w/w	12.1	12.5
Imidized Preform Properties	31.8	34.42
Resin Content (cured), % w/w	11.8	13.3
Volatile Content, % w/w	98	106
Extent of Volatile Expulsion, % w/w [2]		
Composite Properties		
Flexural Strength, MPa (Ksi)		
R.T.	931 (135)	1027 (149)
588°K (600°F)	683 (99)	600 (87)
Flexural Modulus, GPa (Msi)		
R.T.	60 (8.7)	61 (8.8)
588°K (600°F)	61 (8.9)	52 (7.6)
Shear Strength MPa (Ksi)		
R.T.	63 (9.1)	68 (9.8)
588°K (600°F)	39 (5.6)	40 (5.8)
Appearance After Molding [2]	G	E
Flow, % w/w [5]	0.5	1.2
Density, g/cc [6]	1.577	1.570
Resin Content, % w/w	31.99	34.39
Fiber Volume, % v/v	60.94	58.53
Void Volume, % v/v	0.8	0.6

(1) Fresh prepreg was stored at 243°K (-22°F) for a maximum of 10 days.

(2) E (excellent), uniform smooth and free of surface defects.

G (good), some surface discoloration near the periphery of the laminate, no visually detectable porosity

F (fair), general surface discoloration and slight porosity near the periphery of the laminate

P (poor), general surface depressions and porosity
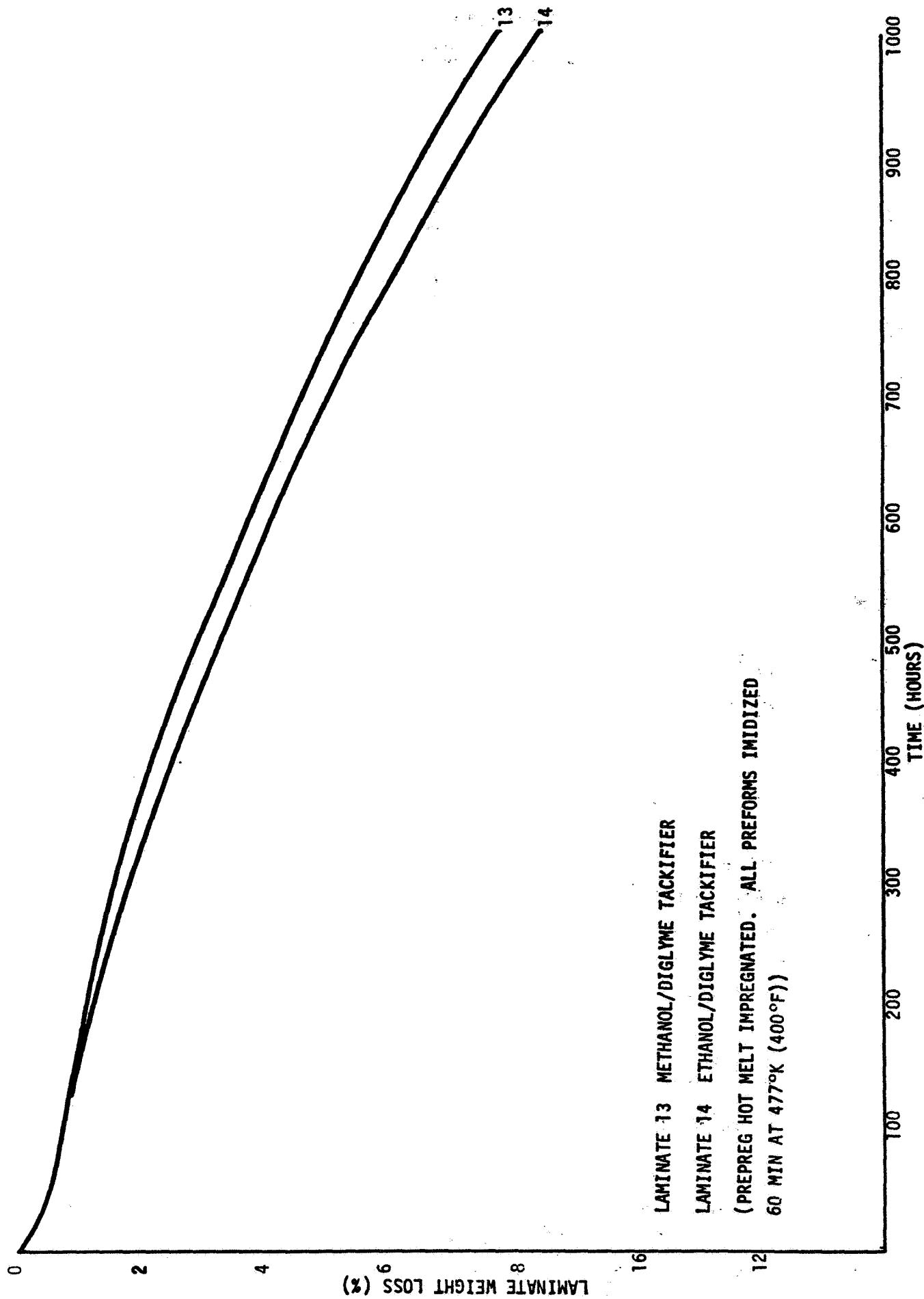
FIGURE 15. WEIGHT LOSS OF IMPROVED TACK PMR/C-3000 CLOTH LAMINATED EXPOSED TO 589°K (600°F)

LAMINATE 13 METHANOL/DIGLYME TACKIFIER

LAMINATE 14 ETHANOL/DIGLYME TACKIFIER

(PREPREG HOT MELT IMPREGNATED. ALL PREFORMS IMIDIZED 60 MIN AT 477°K (400°F))

3.3 GEL PERMEATION CHROMATOGRAPHY STUDIES

The GPC solution studies were attempted to completely identify and possibly quantify all of the monomers, potential side products and adducts, i.e., triesters and tetraesters and nadimides, of the improved tack PMR formulations. The columns, materials and procedures used were identical to those reported by K. E. Reed (Reference 6). In order to verify the identity of the components separated during this study, the individual components, BTDE, NE and MDA, were injected into the columns and their elution times determined. BTDE and NE eluted as reported (Reference 6). However, MDA was retained on the columns, and continual conditioning of the columns with methanol and water did not free the MDA from the columns.

For expediency purposes, the GPC analysis technique was directed to compare triester and tetraester formation in the hot melt and solution versions of the dimethyl ester of BTDA with time on exposure to ambient temperature.

Separation of the components of the dimethyl ester of BTDA, which was prepared by both hot melt (Section 3.2.1) and methanol solution (Section 2.1) techniques, was readily accomplished. These results are summarized in Table 10. Details of the procedures and equipment used and a representative chromotograph is given in Appendix E. For this study, in order to eliminate any batch-to-batch variability, one 50% w/w solution of BTDE in methanol and one 69% w/w solution of BTDE in methanol and one 69% w/w solution of BTDE in diglyme were prepared, and samples of these were stored at room temperature or at $253^{\circ}K$ ($-4^{\circ}F$) for the times shown in Table 10. Storage of BTDE solutions at this reduced temperature has been shown to effectively eliminate the formation of triesters and tetraesters (Reference 5). The components eluting around 300 seconds and 330 seconds have been shown to be the diester and triester of BTDA respectively (Reference 6). The results of this study show that some triester of BTDA has been formed in the hot melt formulation (13278-44-2) during preparation; however, with time the concentration of the higher ester has remained essentially constant. A similar concentration of triester was formed during the preparation of the 50% w/w solution of BTDE in methanol. Also, it was that after 100 days there was a 50% increase of the triester concentration in this solution.

TABLE 10. GPC SOLUTION STUDIES METHYL ESTERS OF BTDA

BTDE SOLUTION	FIGURE NUMBER	TIME AT 253°K (-4°F), DAYS	TIME AT 293°K (68°F), DAYS	ELUTION TIME, SEC	RELATIVE PEAK AREA, %
50% W/W in Methanol 13278-44-1	D-1	103	0	302 343	97.0 3.0
	D-2	0	103	288 326	95.5 4.5
69% W/W	D-3	103	0	291 326	96.1 3.9
	D-4	57	46	302 341	97.3 2.7
In Diglyme	D-5	30	73	297 335	97.5 2.5
13278-44-2	D-6	0	103	292 330	97.1 2.9

4.0 COMPRESSION MOLDING PROCESS DEVELOPMENT USING UNIDIRECTIONAL PREPREG

In this phase of the program the composite mechanical properties of the improved tack PMR system employing the methanol/diglyme solvent system, before and after long term aging at 588°K (600°F), were collected. These results were compared with data for an unmodified PMR-5 composite control in order to identify any potential long term deficiencies with the use of the new system. Unidirectional prepreg was prepared and laminates, 21.6 cm x 21.6 cm x 0.23 cm (8.5 in x 8.5 in x 0.09 in), were molded from material in four different conditions of storage.

Methanol, the conventional carrier solvent for the PMR systems, was selected because in this study there were no significant improvements in the tack characteristics, processability or mechanical properties of the prepregs and composites which employed ethanol as a carrier solvent.

4.1 PREPREG PREPARATION

Unidirectional prepreg was prepared with Celion-6000 continuous fiber yarn. The fibers used for the development of composite data were specially procured from the Celanese Corporation. Two fiber lots were employed; both were surface oxidized but were free of any polymer sizing.

These dry fibers were collimated on a drum with a circumference of 240 cm (94.4 in). Mylar film was used as a backing material. The drum was mounted on a lathe, and the yarn was wrapped upon it at consistent intervals by metering the yarn through the lathe headstock. The yarn was wound at 12 tows per inch; this provided a cured ply thickness of approximately 0.018 cm (0.0072 in). This dimension is representative of commercially prepared materials.

Impregnation was carried out by metering the resin solution onto the fiber surface with a peristaltic pump. By knowing the fiber weight, an appropriate amount of solution was used to provide a cured resin content of 35.0% w/w. In such a manner it was possible to produce unidirectional prepreg with resin contents that were reproducible to $\pm$ 2% w/w, in batch to batch preparation.

The prepreg was then dried 20 to 24 hours on the drum, under a hood at ambient conditions. After this exposure, the prepreg volatile content reaches 12 to 12.5% w/w. This provided the prepreg with promising tack and drape. At this stage the prepreg was either fabricated into laminates, aged at ambient conditions or stored in sealed polyethylene bags at reduced temperatures.

4.2 PREPREG AGING

Prepreg handleability properties of unidirectional tape were determined by employing the same techniques used on the fabric prepregs which were evaluated in Sections 3.1.1 and 3.2.2. Data determined on freshly prepared unidirectional tape and tape aged for thirty days at 278°K (40°F) that the tack life of the unidirectional prepregs averaged fourteen days. This tack life was less than that found with fabric prepreg ($\sim$ 21 days). However, since the unidirectional tape was about one half the thickness of the fabric prepreg (cured ply thickness of 0.018 cm vs. 0.036 cm (0.007 in. versus 0.015 inch), it would be expected that the tackifier had diffused faster through the unidirectional prepreg. This should cause a shorter tack life in the thinner material.

4.3 LAMINATE PROCESSING

The most promising compression molding process cycle identified in Section 3.1 was used to mold the larger [i.e., 21.6 cm x 21.6 cm x 0.23 cm (8.5 in x 8.5 in x 0.090)] composites in this task. All possessed some surface areas of incomplete prepreg consolidation ($\sim$ 10% of the total area). These laminates were sectioned, polished and examined microscopically. Sections which exhibited the most severe surface flaws had interior macrovoids, 0.025 - 0.0025 cm (0.01 - 0.001 in.) in dimesion, filling approximately 2% to 5% of the volume. Sections which had smooth laminate surfaces had very low apparent void volumes (based on visual examination these were less that 0.5% v/v). The resin flow of the laminate, i.e., the weight of the resin flash divided by the laminate weight, was less than 0.4% w/w. Apparently this low flash level was insufficient for total consolidation of the composite to occur.

In order to obtain increased resin flow during molding, an alternative molding cycle was employed. This cycle, recommended by the program manager at NASA Lewis Research Center, provides a much higher mold heating rate and allows the resin to obtain a higher temperature and lower viscosity before gelation. This change in the process cycle provided the necessary higher resin flow. The modified cycle is summarized in the following steps:

(1) Imidize preform in an air circulating oven for 60 minutes at 477°K (400°F)

(2) Place the preform in a mold, both of which are at ambient temperature

(3) Attach a thermocouple to the preform

(4) Place the mold in a press which has been preheated to 603°K (625°F) and apply contact pressure

(5) When the laminate temperature reaches 505°K (450°F) at a rate between 22°C/min and 44°C/min (40°F/min and 80°F/min) apply 4.8 MPa (700 psi)

(6) When the laminate reaches 561°K (550°F) reduce the press temperature to 599°K (600°F)

(7) Hold at 588°K (600°F) for one hour

(8) Cool laminate to 505°K (450°F) under full pressure and then cool to room temperature under contact pressure

(9) Postcure at 588°K (600°F) for 16 hours

For devolatilization and imidization, twelve plies of prepreg, 21.6 x 21.6 cm (8.5 x 8.5 in) were placed between two pieces of porous teflon coated release fabric and two pieces of 181 style E glass. Caul sheets of thin aluminum were used for support on top and bottom of the preform stops, 0.64 cm (0.25 in) thick, were placed between these sheets, and a weight, ∿ 0.5 Kg (1 lb.) was placed upon the top caul. This was done to

eliminate any positive pressure upon the preform during the initial stages of imidization. At this stage the resin was very fluid so that fiber washing of the prepreg would occur upon the application of even a slight positive pressure. A time and temperature profile was plotted using a Hewlett Packard Model 680 strip chart recorder for all preforms and laminates. Temperature precision was maintained within $\pm$ 1% °K/°K, and time precision was maintained within $\pm$ 10% min/min during the imidization and molding processes. Cured laminate thickness was 0.218 cm (0.086 in.) $\pm$ 0.005 cm (0.002 in.).

By using this process it was possible to obtain laminates which were 100% consolidated. Cross sections showed no appreciable voids. Resin flow of these laminates was about 1% w/w. This was roughly twice that of laminates made using the original cure cycle which employed a slower heating rate.

In addition, several control laminates were fabricated using the conventional PMR-15 system. Unidirectional C-6000 prepregs were prepared using materials and techniques identical to the improved tack PMR/C-6000 prepreg, with the exception of the omission of the diglyme. The modified fast heating rate, cure cycle was used to fabricate these large laminates. These laminates exhibited significantly higher flow, about 2% w/w, than the improved tack PMR laminates. The higher resin flash completely filled the mold cavity.

A cursory examination of the melt behavior of the PMR-15 control and improved tack PMR powders, which were imidized for one hour at 477°K (400°F), showed significant differences in the viscosity of these materials. When the PMR-15 control powder instantly melted and became almost watery in nature while the improved tack PMR powder melted but appeared to be of a honey-like consistency. Based upon these qualitative observations, it appears that the viscosity of the improved tack PMR material was significantly higher than that of the PMR-15.

4.4 LAMINATE EVALUATION

The data reflecting the quality, thermal stability, physical properties and mechanical properties of the large 21.6 cm x 0.23 (8.5 in x 8.5 in x 0.09 in), unidirectional laminates selected for this study are presented in Tables 11 through 15. Included in Table 11 are data for the PMR-15

control laminate, while in Tables 12 through 15 present data for improved tack PMR laminates. The improved tack PMR prepregs were conditioned for four different periods as is noted on the tables. These specimens were tested after a 16 hour postcure at 588°K (600°F) and after isothermal aging for 300, 600 and 1000 hours at 588°K (600°F). The physical properties of all the specimens were excellent with fiber volumes in the 57% to 61% v/v range and void volumes less than 1% v/v. The mechanical properties, at 588°K (600°F), of the improved tack PMR/C-6000 laminates were 10% to 15% higher than those of the PMR-15 control laminate.

4.4.1 Ultrasonic C-Scan Inspection

All of the large unidirectional laminates fabricated were subjected to ultrasonic C-scan inspection. This evaluation was performed by Sonic Engineering Inc., in South Gate, California, a firm which specializes in non-destructive testing. Representative C-scans of the nine laminates which were selected for further evaluation are given in Appendix F. All of these laminates were processed using a press preheated to 588°K (600°F) to obtain a heating rate rapid enough to provide resin flow adequate for complete laminate consolidation. Even though visual inspection indicated that these appeared to be high quality laminates, the ultrasonic inspection revealed relatively small void defects to be present in some of the laminates. Only about 50% of the area of each set of two laminates for each prepreg aging condition was required for evaluation. These small defect areas were removed and only laminate specimens containing zero defects were employed in long term aging studies.

Table 11. PROPERTIES OF IMPROVED TACK PMR/C-6000 UNIDIRECTIONAL LAMINATES METHANOL SOLVENT (PMR-15 CONTROL) FRESH PREPREG				
Composite No.	18			
C-600 Fiber Lot No.	WTA-7-9Y-31			
Ultra Sonic C Scan Figure No.	F-1			
Prepreg Properties				
Resin Content (cured), % w/w	35.41			
Volatile Content, % w/w	9.57			
Imidized Preform Properties				
·Resin Content (cured), % w/w	35.28			
Volatile Content, % w/w	9.21			
Extent of Volatile Expulsion, % w/w	96.2			
Composite Properties				
Aging Time at 588°K (600 F), hr.	0	300	600	1000
Composite Section	18	18	18	18
Flexural Strength, MPa (ksi) [1]				
R. T.	2013 (292)			
588°K (600°F)	1014 (147)	1262 (183)	1151 (167)	1069 (155)
Flexural Modulus, GPa (Msi)				
R. T.	116 (16.8)			
588°K (600°F)	104 (15.1)	108 (15.6)	108 (15.6)	104 (15.1)
Shear Strength, MPa (ksi) [2]				
R. T.	127 (18.4)			125 (18.2)
588°K (600°F)	56 (8.1)	66 (9.5)	63 (9.2)	60 (8.7)
Weight Loss, %	0	0.86	2.29	4.40
TMA Figure No.	C-17	C-18	C-19	C-20
Glass Transition Temperature, °K (°F)	606 (631)	599 (619)	612 (642)	609 (637)
Density, g/cc	1.583	1.586	1.590	1.584
Resin Content, % w/w	35.08	34.79	32.99	32.46
Fiber Volume, % v/v	58.40	58.74	60.52	60.78
Void Volume, % v/v	-0.47	-0.54	-0.25	-0.25

(1) Triplicate specimens.
(2) Quintuplet specimens.

Table 12.

Table 12. PROPERTIES OF IMPROVED TACK PMR/C-6000 UNIDIRECTIONAL LAMINATES METHANOL/DIGLYME SOLVENT SYSTEM(80/20 PBW) FRESH PREPREG

	9	14			
Composite No.	9	14			
C-600 Fiber Lot No.	HTA-7-9Y31	HTA-7-9Y31			
Ultra Sonic C Scan Figure No.	F-2	F-3			
Prepreg Properties					
Resin Content (cured), % w/w	34.55	35.42			
Volatile Content, % w/w	12.29	12.53			
Imidized Preform Properties					
Resin Content (cured), % w/w	35.46	35.57			
Volatile Content, % w/w	12.02	11.38			
Extent of Volatile Expulsion, % w/w	97.8	90.8			
Composite Properties					
Aging Time at 588°K (600°F), hr.	0	0	300	600	1000
Composite Section	9	14	14	14	14
Flexural Strength, MPa (ksi) (1)					
R. T.	2103 (305)	1248 (181)	1269 (184)	1179 (171)	1041 (151)
588°K (600°F)	1138 (165)				
Flexural Modulus, GPa (Msi)					
R. T.	114 (16.6)	112 (16.3)	115 (16.7)	106 (15.4)	108 (15.7)
588°K (600°F)	108 (15.7)				
Shear Strength, MPa (ksi) (2)					
R. T.	58 (8.4)	61 (8.8)	68 (9.8)	67 (9.7)	63 (9.2)
588°K (600°F)					
Weight Loss, %	0	0	1.05	2.57	4.51
TMA Figure No.		C-21	C-22	C-23	C-24
Glass Transition Temperature, °K (°F)		605 (630)	597 (615)	614 (646)	625 (666)
Density, g/cc	1.592	1.596	1.593	1.584	1.576
Resin Content, % w/w	35.08	34.43	33.51	33.73	32.64
Fiber Volume, % v/v	58.70	59.47	60.19	59.63	60.31
Void Volume, % v/v	-1.01	-1.12	-0.65	-0.09	0.73

(1) Triplicate specimens.

(2) Quintuplet specimens.

Table 13. PROPERTIES OF IMPROVED TACK PMR/C-6000 UNIDIRECTIONAL LAMINATES METHANOL/DIGLYME SOLVENT SYSTEM (80/20 PBW) PREPREG AGED 30 DAYS AT 278°K (40°F)

	13	12			
Composite No.					
C-600 Fiber Lot No.	HTA-7-9Y31	HTA-7-9Y31			
Ultra Sonic C Scan Figure No.	F-4	F-5			
Prepreg Properties					
Resin Content (cured), % w/w	34.63	34.63			
Volatile Content, % w/w	12.27	12.27			
Imidized Preform Properties					
Resin Content (cured), % w/w	35.75	35.63			
Volatile Content, % w/w	11.99	12.01			
Extent of Volatile Expulsion, % w/w	97.7	97.9			
Composite Properties					
Aging Time at 588°K (600°F), hr.	0	0	300	600	1000
Composite Section	3	12	12	13	13
Flexural Strength, MPa (ksi)[1]					
R. T.	1986 (288)	1186 (172)	1338 (194)	1138 (165)	1055 (153)
588°K (600°F)	1158 (168)				
Flexural Modulus, GPa (Msi)					
R. T.	110 (15.9)	108 (15.6)	111 (16.1)	105 (15.3)	101 (14.7)
588°K (600°F)	105 (15.3)				
Shear Strength, MPa (ksi)[2]					
R. T.	131 (19.0)	61. (8.8)	67 (9.7)	69 (10.0)	65 (9.4)
588°K (600°F)	60 (8.7)				
Weight Loss, %	0	0	1.05	2.44	5.03
TMA Figure No.		C-25			
Glass Transition Temperature, °K (°F)		606 (631)			
Density, g/cc	1.591	1.591	1.594	1.583	1.579
Resin Content, % w/w	36.01	35.02	34.19	34.89	34.00
Fiber Volume, % v/v	57.83	58.59	59.60	58.56	59.20
Void Volume, % v/v	-1.23	-1.03	-0.90	-0.40	0.13

(1) Triplicate specimens.
(2) Quintuplet specimens.

Table 14. PROPERTIES OF IMPROVED TACK PMR/C-6000 UNIDIRECTIONAL LAMINATES METHANOL/DIGLYME SOLVENT SYSTEM (80/20 PBW) PREPREG AGED 14 DAYS AT R.T.

Composite No.	11	10			
C-600 Fiber Lot No.	HTA-7-9Y31	HTA-7-8112			
Ultra Sonic C Scan Figure No.	F-6	F-7			
Prepreg Properties					
Resin Content (cured), % w/w	35.4	35.4			
Volatile Content, % w/w	11.11	11.11			
Imidized Preform Properties					
Resin Content (cured), % w/w	35.40	36.21			
Volatile Content, % w/w	10.51	10.91			
Extent of Volatile Expulsion, % w/w	94.6	98.2			
Composite Properties					
Aging Time at 588°K (600°F), hr.	0	0	300	600	1000
Composite Section	11	10	10	10	10
Flexural Strength, MPa (ksi)[1]					
R.T.	1806 (262)	1214 (176)	1220 (177)	1138 (165)	1034 (150)
588°K (600°F)	1193 (173)				
Flexural Modulus, GPa (Msi)					
R.T.	111 (16.1)	105 (15.2)	106 (15.4)	96 (13.9)	98 (14.2)
588°K (600°F)	103 (15.0)				
Shear Strength, MPa (ksi)[2]					
R.T.	125 (18.2)	61 (8.9)	70 (10.1)	68 (9.8)	62 (9.0)
588°K (600°F)	63 (9.2)				
Weight Loss, %	0	0	1.08	2.93	6.02
TMA Figure No.		C-26			
Glass Transition Temperature, °K (°F)		594 (610)			
Density, g/cc	1.596	1.574	1.565	1.560	1.568
Resin Content, % w/w	35.23	36.57	36.17	36.07	34.58
Fiber Volume, % v/v	58.74	56.72	56.78	56.66	58.30
Void Volume, % v/v	-1.34	-0.30	0.33	0.70	0.61

(1) Triplicate specimens.
(2) Quintuplet specimens.

Table 15. PROPERTIES OF IMPROVED TACK PMR/C-6000 UNIDIRECTIONAL LAMINATES METHANOL/DIGLYME SOLVENT SYSTEM (80/20 PBW) PREPREG AGED 30 DAYS AT 278°K (40°F) AND 14 DAYS AT R.T.

Composite No.	16		17		17
C-600 Fiber Lot No.	HTA-7-8112 F-8		HTA-7-8112 F-9		HTA-7-8112 F-9 F-9
Ultra Sonic C Scan Figure No.					
Prepreg Properties					
Resin Content (cured), % w/w	34.35		34.35		
Volatile Content, % w/w	11.4		11.4		
Imidized Preform Properties					
Resin Content (cured), % w/w	35.72		36.10		
Volatile Content, % w/w	10.79		10.83		
Extent of Volatile Expulsion, % w/w	94.7		95.0		
Composite Properties					
Aging Time at 588°K (600°F), hr.	0	0	300	600	600
Composite Section	16	17	17	17	17
Flexural Strength, MPa (ksi) [1]					
R. T.	1731 (251)	1255 (182)	1386 (201)	1186 (172)	1062 (154)
588°K (600°F)	1303 (189)				
Flexural Modulus, GPa (Msi)					
R. T.	117 (16.8)	108 (15.7)	112 (16.3)	105 (15.2)	97 (14.0)
588°K (600°F)	112 (16.3)				
Shear Strength, MPa (ksi) [2]					
R. T.	130 (18.9)	63 (9.1)	70 (10.2)	71 (10.3)	64 (9.3)
588°K (600°F)	57 (8.3)				
Weight Loss, %	0	0	1.09	2.43	5.38
TMA Figure No.		C-27			
Glass Transition Temperature, °K (°F)		602 (624)			
Density, g/cc	1.576	1.573	1.570	1.527	1.575
Resin Content, % w/w	34.96	34.87	35.62	34.37	34.07
Fiber Volume, % v/v	58.24	58.21	57.43	58.71	58.99
Void Volume, % v/v	0.01	0.24	0.20	0.48	0.37

(1) Triplicate specimens.

(2) Quintuplet specimens.

4.4.2 ISOTHERMAL GRAVIMETRIC ANALYSIS

Isothermal gravimetric analyses were conducted on laminate plaques, size 10.2 x 10.2 x 0.23 cm (4.0 x 4.0 x 0.90 in.) taken from composites molded from the PMR-15 control prepreg and from the improved tack PMR prepregs. The weight loss data shown in Figure 16 represents average values for each set of laminate plaques. As can be seen in Figure 16, the tackifier, diglyme, has not had an adverse effect upon the thermal stability of these PMR laminates. In addition, the aging of the improved tack prepreg had no noticable effect upon laminate weight loss at this elevated temperature. The improved tack PMR laminate plaques lost roughly 4.5% to 6% of their initial weight after 1000 hours of aging at 588°K (600°F) while the PMR-15 control lost 4.5% of its weight. Similar aging studies on PMR-15/C-6000 laminates conducted at NASA Lewis Research Center, which have recently been published (Reference 7), show nearly identical results [$i.e.$, weight losses in the 4% to 6% range after 1000 hours exposure to 588°K (600°F)].

4.4.3 LAMINATE PHYSICAL PROPERTIES

The resin contents of the short beam shear specimens machined from the laminate plaques examined in this study were determined by acid digestion techniques. The densities of these specimens were found by water displacement methods. These data were used to calculate the fiber volumes and void volumes of the various samples. As can be seen from the data in Tables 11 through 15, all of the void volumes were low, less than 1% v/v, and indicative of high quality laminates. Some of these values were less than zero; they all corresponded to laminates fabricated using the fiber lot HTA-7-9Y31. It is quite probable that the cause of anomaly was lot-to-lot variability of the fiber density. Celanese product literature quote fiber densities as typically being 1.77 g/cc (0.064 lb/in^3) and, as a minimum, at least 1.72 g/cc (0.062 lb/in^3). In this study a value of 1.76 glcc (0.0635 lb/in^3) was employed. It is quite likely that fiber lot HTA-7-9Y31 had a density close to 1.80 g/cc (0.065 lb/in^3). This value would have provided consistent void volume values, $i.e.$, between 0% and 1% v/v, for all laminates containing the HTA-7-9Y31 fiber lot. Such variation in fiber density would have slight effect upon the reported fiber volumes; laminates employing the denser fibers would have
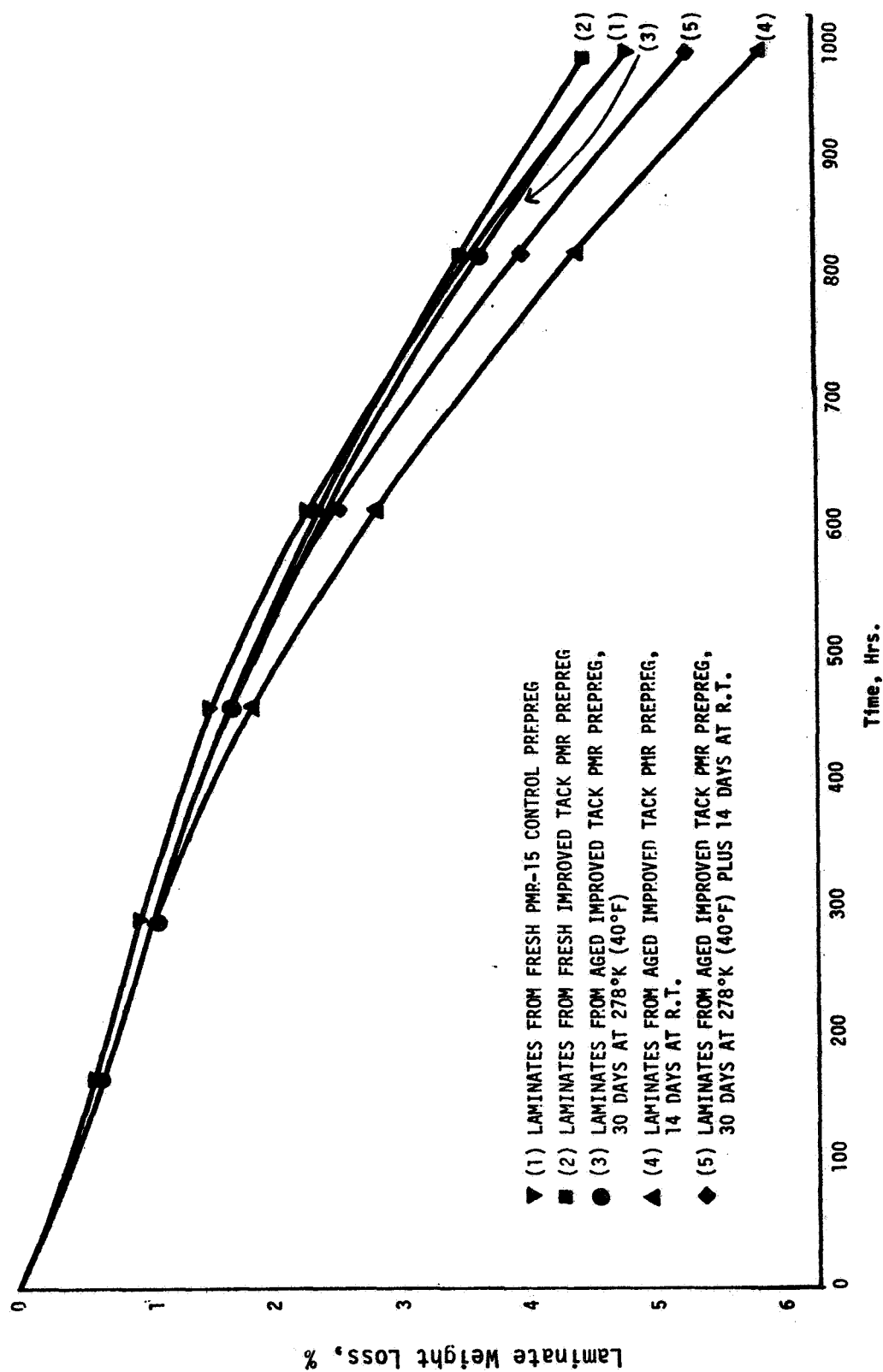
Figure 16. Weight Loss of Improved Tack PMR/C-6000 Unidirectional Laminates Exposed to 588°K (600°F)

- (1) LAMINATES FROM FRESH PMR-15 CONTROL PREPREG
- (2) LAMINATES FROM FRESH IMPROVED TACK PMR PREPREG
- (3) LAMINATES FROM AGED IMPROVED TACK PMR PREPREG, 30 DAYS AT 278°K (40°F)
- (4) LAMINATES FROM AGED IMPROVED TACK PMR PREPREG, 14 DAYS AT R.T.
- (5) LAMINATES FROM AGED IMPROVED TACK PMR PREPREG, 30 DAYS AT 278°K (40°F) PLUS 14 DAYS AT R.T.

fiber volumes about 1% to 2% v/v lower than reported. However, even if this was the case, the fiber volumes of all of these specimens were within the program objective of 59% ± 2% v/v. This consistency should allow for reliable comparison of the laminates mechanical properties.

A sufficient number of improved tack PMR laminates were fabricated to demonstrate reproducibility. As can be seen from the data in Tables 11 through 15 two laminates were molded for each prepreg aging condition. Parallel evaluations of post cured only specimens from these pairs of laminates have demonstrated reproducibility in terms of fiber volume, void volume and elevated temperature flexure and shear strengths.

TMA analysis of a select number of these specimens was performed. The apparent glass transition temperatures of these composites are reported in Tables 11 through 15, and a representative expansion profile is given in Appendix C. Inspection of the reported Tg's shows that there is no detectable difference in the thermal temperatures between the improved tack PMR and PMR-15 control composites. However, there appeared to be a correlation in the apparent glass transition temperature and the type of material analyzed. This is highlighted in Table 16.

TABLE 16. TYPICAL GLASS TRANSITION TEMPERATURES
OF BULK AND REINFORCED PMR MATERIALS

MATERIAL	TYPICAL Tg RANGE
Bulk Resin	613-623 $^\circ$K (644-662°F)
Unidirectional Composite	594-605 $^\circ$K (612-630°F)
Woven Composite	543-588 $^\circ$K (518-600°F)

A rationale for these variations in Tg was discussed in Section 3.1. This involved suspected matrix failure on a microstructural level due to induced thermal stress in the composite.

4.4.4 LAMINATE MECHANICAL PROPERTIES

The effect of isothermal aging at 588°K (600°F) upon the elevated temperature mechanical properties of the laminates is graphically presented in Figures 17 through 19. The properties of the PMR-15 control
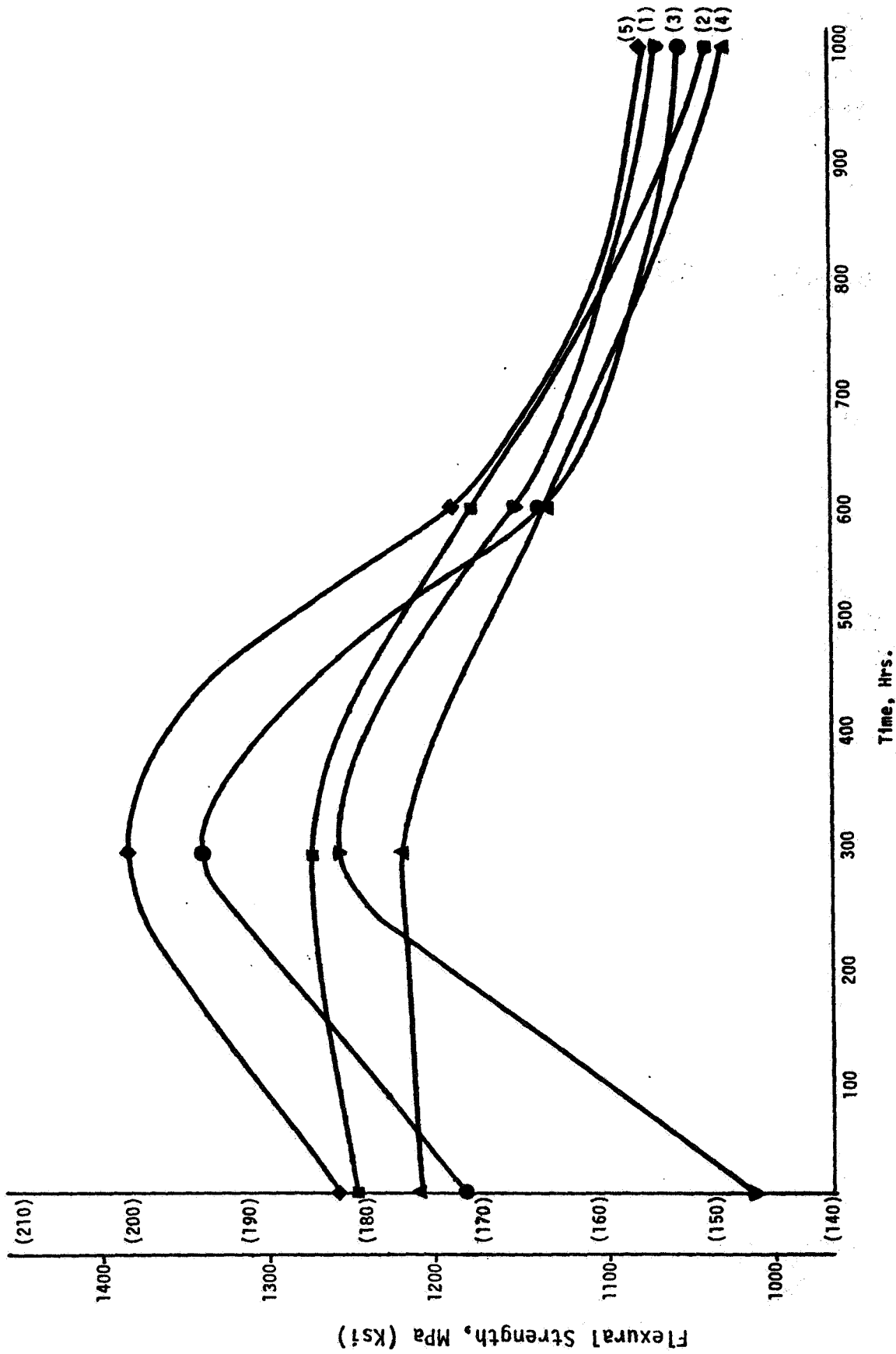
Figure 17 Flexural Strength of Improved Tack PMR/C-6000 Unidirectional Laminates Exposed to 588°K (600°F) (Specimen Identification Shown in Figure 29)
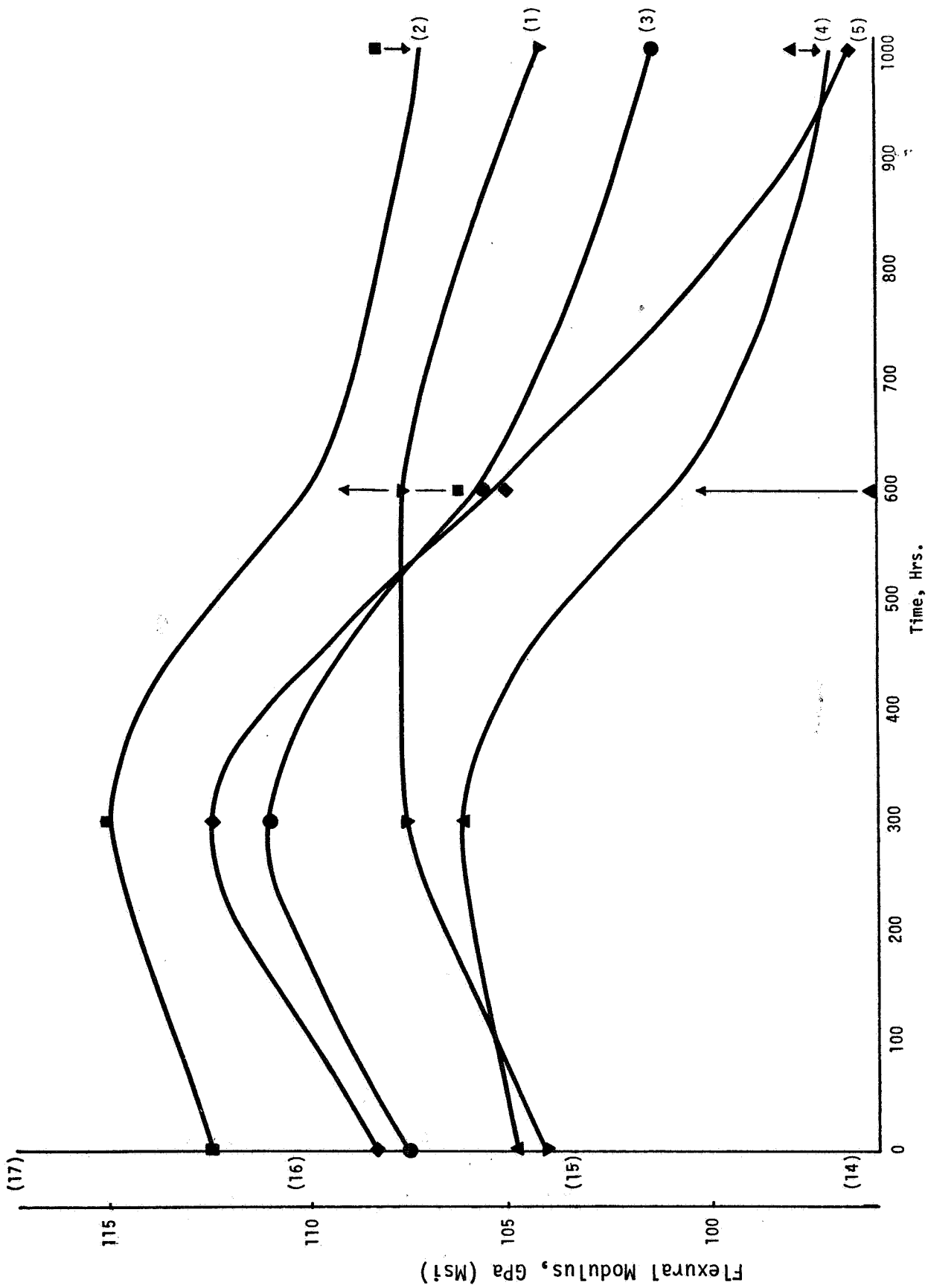
Figure 18   Flexural Modulus of Improved Tack PMR/C-6000 Undirectional Laminates Exposed to 588°K (600°F). (Specimen Identification Shown in Figure 29)
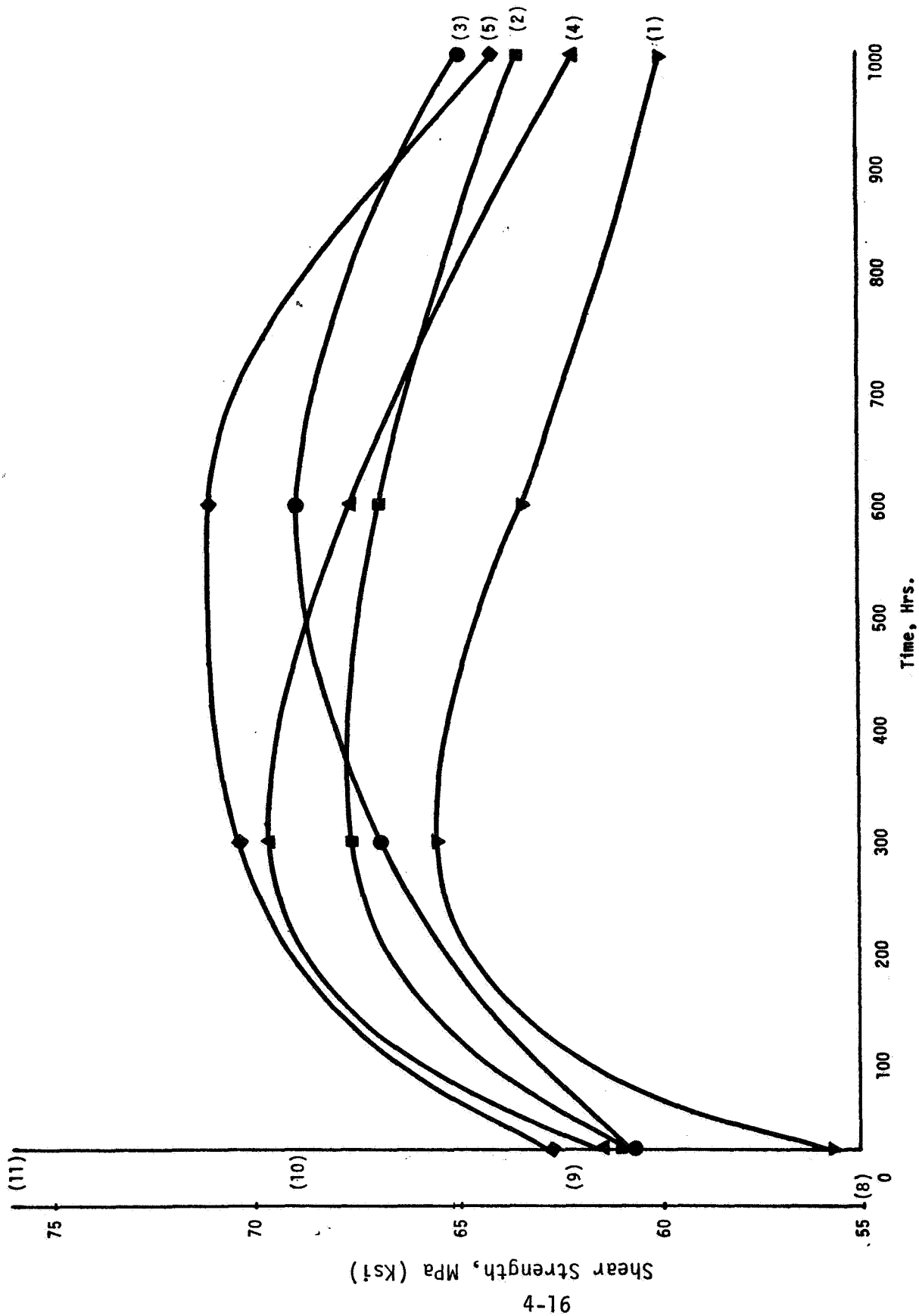
4-15

Figure 19 Shear Strength of Improved Tack PMR/C-600 Unidirectional Laminates Exposed to 588°K (600°F) (Specimen Identification Shown in Figure 29)

4-16

specimens found in this study were quite similar to those recently
reported by Vannucci (Reference 7). The change in flexural strength
and modulus with exposure time are given in Figures 17 and 18. These
properties are highly fiber dependent and usually exhibit a large
degree of scatter so the curves plotted in these graphs should only
be interpreted to indicate trends. The most obvious trend seen in
these plots is the initial increase in elevated temperature flexural
strength and modulus, at about 300 hours of exposure, and the steady
decrease thereafter. The change of the elevated temperature interlaminar
shear strength of these specimens with exposure time is shown in
Figure 19. This property is much more resin dependent, less subject to
data scatter and gives a better indication of the integrity of the
PMR matrix. As can be clearly seen in Figure 19, the interlaminar shear
strengths of all the improved tack PMR specimens were 10% to 15% higher
than the PMR-15 control specimens. The standard deviations experienced
in these tests were usually between 2% to 4%, and the reproducibility
of shear properties among the various improved tack PMR interlaminar
shear strengths do not seem attributable to statistical variation or
inconsistent laminate quality. This difference could be attributed to
differing polymer structures or to improved resin/fiber bonding as a
result of improved flow exhibited by the diglyme system during
imidization.

5.0 AUTOCLAVE MOLDING PROCESS DEVELOPMENT

Autoclave processing methods were shown to be capable of producing high quality composites from improved tack PMR prepregs in this task. These methods were amenable to the procedures necessary for the fabrication of large and complex pieces of hardware. Several 15.2 cm x 10.2 cm x 0.23 cm (6.0 in x 4.0 in x 0.09 in) laminates, using a variety of processing cycles, were fabricated. Composite performance was ascertained through select mechanical and physical tests. Both solution and hot melt coated C-3000 fabric prepregs were utilized in this study to fabricate laminates.

5.1 SOLUTION COATED PREPREG EVALUATION

PMR-15 solutions employing either the methanol (PMR-15 control), methanol/diglyme or ethanol/diglyme solvent systems were used to prepare the fabric prepregs evaluated in this section. Substantial modification of the lay-up procedures and cure cycles normally used to autoclave process conventional PMR prepregs (Reference 8) were necessary to process the improved tack PMR prepregs into high quality composites. However, these modified procedures did not require deviation from the conventional maximum temperature and pressure, $588^{\circ}K$ ($600^{\circ}F$) and 1.4 MPa (200 psi), needed to process PMR-15 prepregs.

5.1.1 LAMINATE PROCESSING

The determination of the autoclave processing parameters have been dictated by previous experience with the PMR-15 system (References 8 and 9). In addition, observations made during the compression molding process study on the effect of the tackifier, diglyme, upon the moldability of the improved tack PMR prepregs have been considered in defining parameters. The most apparent, critical, processing characteristics of the improved tack system are summarized below.

- The improved tack, monomeric, PMR resin, *i.e.*, with diglyme present and prior to appreciable condensation, is of much lower viscosity than the conventional PMR-15 monomeric resin. As such, it is difficult to control the flow of of the improved tack PMR system at this stage.

- When the condensation reactions occur in the presence of diglyme, the resultant imidized improved tack PMR resin appears to be of significantly higher viscosity than the imidized conventional PMR-15 resin.

- Under reduced vapor pressure conditions, *i.e.*, vacuum bag processing, and moderate temperatures, less than $395^{\circ}K$ ($250^{\circ}F$), diglyme can be removed from the system. Upon examination of the vapor pressure of diglyme with temperature, data indicate that at $395^{\circ}K$ ($250^{\circ}F$) a vacuum of at least 20 mm Hg would be necessary to significantly reduce the diglyme concentration. Early removal of significant amounts of diglyme might result in an increase in the amount of flow of the imidized improved tack PMR system. This assumes that a thermodynamic equilibrium state exists in the vacuum bag, *i.e.*, the migration of diglyme would not be diffusion controlled.

- Prepolymer condensation reactions occur most readily in the $395^{\circ}K$ ($250^{\circ}F$) to $450^{\circ}K$ ($350^{\circ}F$) temperature range, necessitating adequate laminate venting and volatile removal.

- A rapid laminate heating rate, greater than
  $3^{\circ}C/min$ ($6^{\circ}F/min.$), after volatile removal
  and autoclave pressurization is required
  to achieve adequate resin flow for composite
  consolidation.

- The achievement of a composite temperature
  of $588^{\circ}K$ ($600^{\circ}F$) for at least one hour is
  needed for adequate matrix crosslinking.

The vacuum bagging technique, which was used to fabricate all of
the autoclave molded laminates, is shown in Figure 20. This design
was conceived after consideration of the anticipated most critical
processing parameters. A key material used in this lay up is the
gas permeable and resin impermeable Celgard, polypropylene, film. By
employing this film the very low viscosity monomeric resin was confined
to the laminate while the necessary volatile expulsion was accomplished
under full vacuum bag pressure, i.e., 97kPa (14 psi) external atmospheric
pressure and less than 20 mm (0.8 in) vapor pressure. As the cure cycles
passed $450^{\circ}K$ ($350^{\circ}F$) the Celgard melted and decomposed. However,
sufficient resin condensation had taken place so that resin flow was low
enough that the 181 glass fabric breather remained porous to the small
amount of remaining volatile matter.

The cure cycles used in this study have been graphically represented
in Figures 21 through 24. Many processing parameters have been held
constant during this study. These include the use of full vacuum bag
pressure throughout the cycle, the attainment of rapid heating rates
during the cross linking stages of the polymerization, at least $5^{\circ}K$
($8^{\circ}F$) per minute, the initiation of autoclave pressurization when the
laminate reaches $505^{\circ}K$ ($450^{\circ}F$), the attainment of 1.4 MPa (200 psi) auto-
clave pressure upon the laminate reaching $533^{\circ}K$ ($500^{\circ}F$) and the curing of
the laminate for one hour at $588^{\circ}K$ ($600^{\circ}F$). The parameters varied in
this study were the times and temperatures of the dwell cycles. The
purpose was to define the minimum conditions necessary to remove enough
condensation products and solvents from the lay-up so that voids would not
form in the laminate during the cross linking stage of the cure cycle.
In addition, it was felt that defining a minimum dwell temperature would be
desirable to obtain adequate resin flow after the pressurization of the

Kapton bag

2 plies 181 glass fabric

Aluminum caul plate 0.32 cm (0.125 in)

Non-porous TFE coated glass fabric

181 glass fabric

Celgard 4510 film

Porous TFE coated glass fabric

Laminate

Porous TFE coated glass fabric

Celgard 4510 film

181 glass fabric

Non-porous TFE coated glass fabric

Schnee Morehead 5120-C silicone sealant

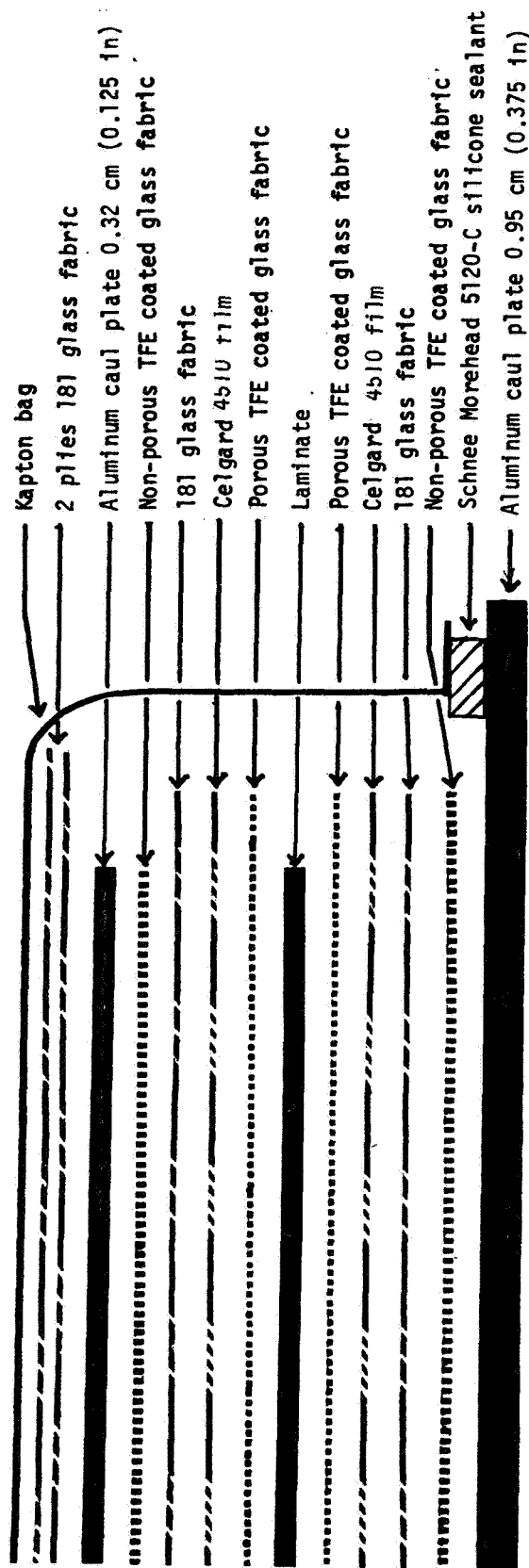Aluminum caul plate 0.95 cm (0.375 in)

Figure 20 Schematic of Vacuum Bag Lay Up
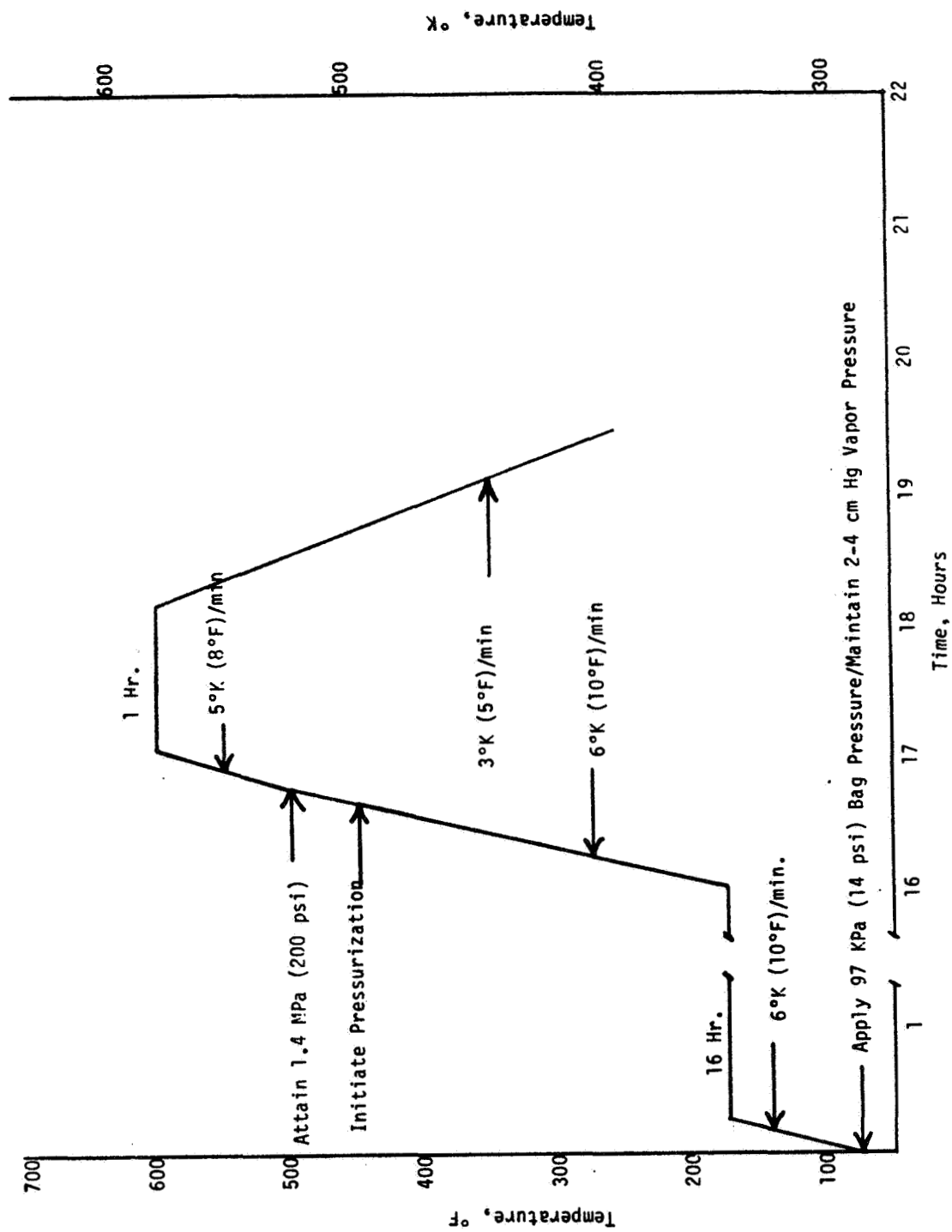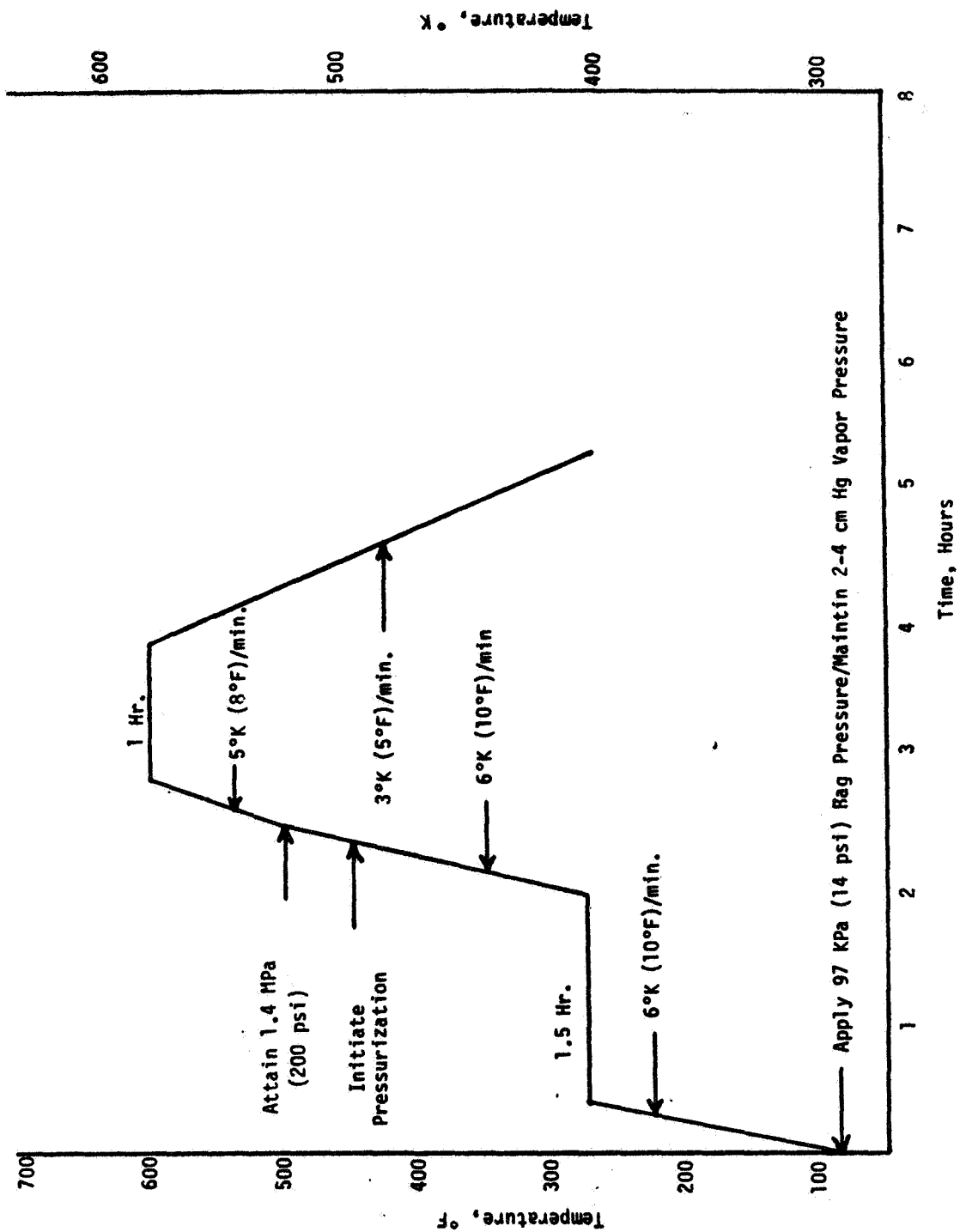
Figure 21 Autoclave Cure Cycle A-1
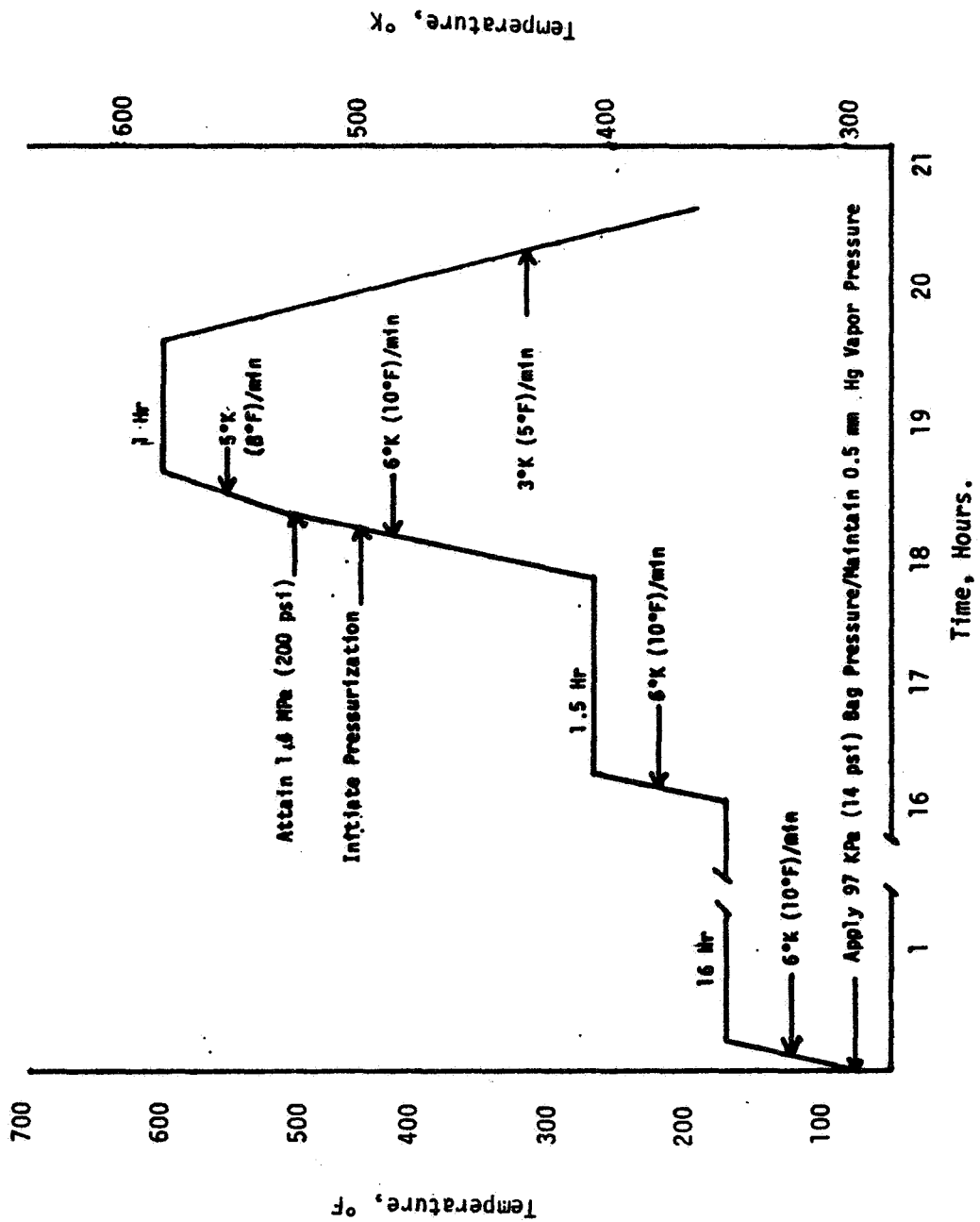
Figure 22 Autoclave Cure Cycle A-2

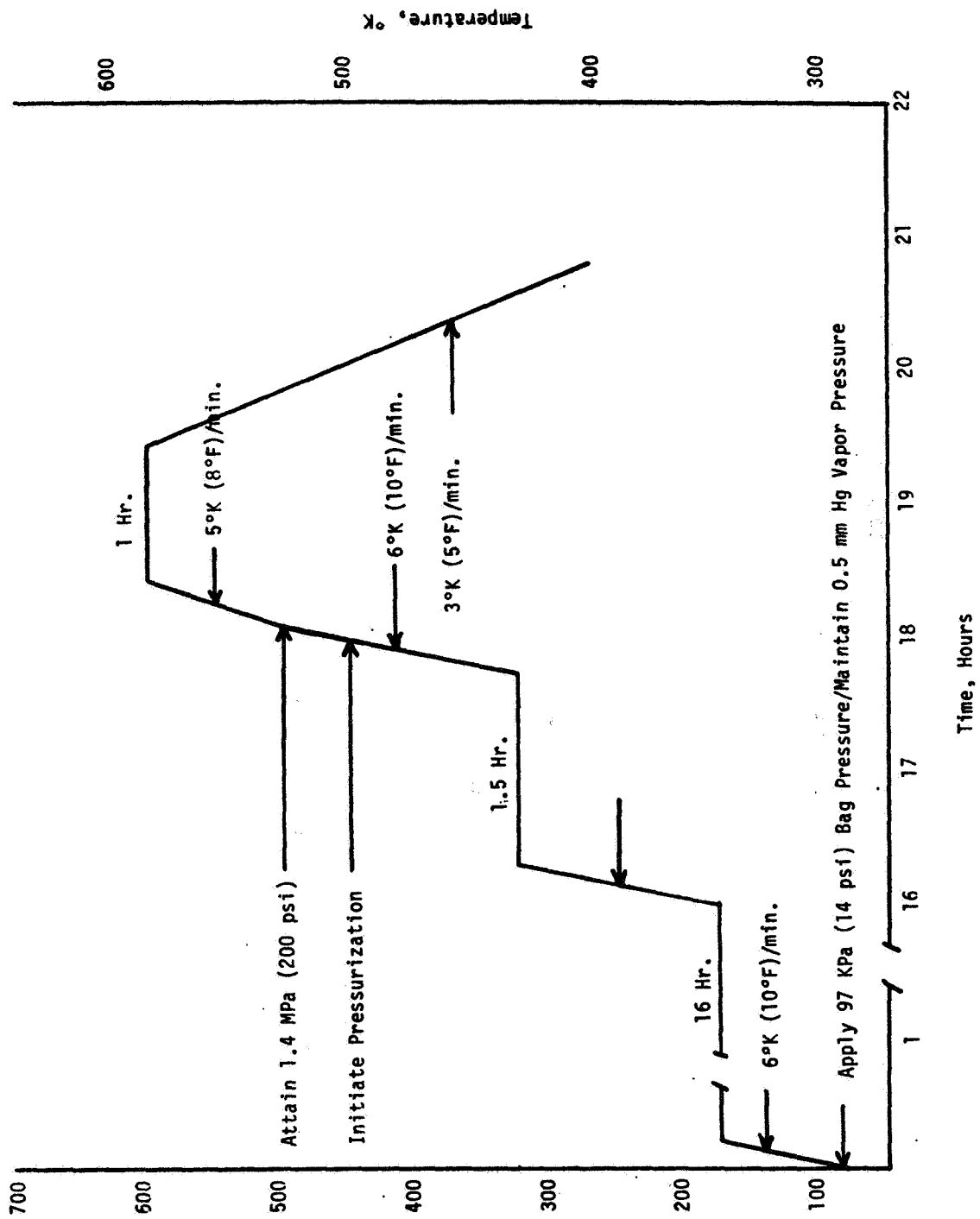Figure 23 Autoclave Cure Cycle A-3

5-7

Figure 24 Autoclave Cure Cycle A-4.

autoclave. As can be seen in the cure cycle schematics, the temperature and duration of the dwell steps increase from Figures 21 through 24.

The mechanical and physical properties of the laminates fabricated from solution coated C-3000 cloth prepreg are given in Tables 16 through 18. In addition, volatile products escaping from the lays were collected and their weights recorded after various steps of the cure cycles. Data for laminates employing the methanol/diglyme solvent system and the ethanol/diglyme solvent system are given in Tables 16 and 17, respectively. Two laminates using methanol only as a solvent (PMR-15 control) were also fabricated for comparative purposes; data for these are given in Table 18.

Volatile matter was collected and quantitatively recorded in order to establish the efficiency of the various dwell steps for the removal condensation products and solvents. This was done by condensing the volatile matter in a dry ice/isopropanol cold trap. Cursory inspection of weights of the volatile matter collected during the dwell steps of each lay-up compared to the total weight of volatile matter collected, indicates that at least 75% of the volatile matter must be removed in a dwell cycle in order to obtain relatively low void content laminates.

In addition several conclusions can be made regarding the expulsion of diglyme from the improved tack prepregs by comparing the volatile matter data in Tables 16 and 18; these are:

- A dwell cycle of 16 hours at $353^{o}K$ ($175^{o}F$) was sufficient to remove about 80% of the total volatile matter from PMR-15 control prepreg (Table 18, composite number 10 or 11). This indicates that substantial imidization had taken place at this temperature.

- A similar dwell cycle using improved tack PMR prepreg (Table 16, composite number 3, 5 or 7) removes about the same weight of volatile matter; however, this is only about 30% of the total volatile content. Since the weights of these volatile products were similar, the composition

TABLE 16 AUTOCLAVE MOLDING PROCESS STUDY METHAROL/DIGLYME SOLVENT SYSTEM (80/20 p.b.w.)

	A-1	A-2	A-3	A-4
Cure Cycle Number				
Composite No.	3	1	5	7
Dwell Temperature °K (°F)	353 (175)	408 (275)	353 (175)	353 (175)
Time, hour (1)	16	1.5	16	16
Volatiles, g	3.4	8.8	3.5	3.2
Dwell Temperature, °K (°F)	---	---	408 (275)	436 (325)
Time, hour	---	---	1.5	1.5
Volatiles, g	---	---	7.3	8.5
Total Volatiles Collected, g	12.0	11.5	12.8	12.8
Composite Properties				
Flexural Strength, MPa (Ksi)				
R.T.	455 (66)	646 (94)	883 (128)	834 (121)
588°F (600°F)	386 (56)	450 (65)	669 (97)	585 (85)
Flexural Modulus, MPa (Ksi)				
R.T.	47 (6.2)	49 (7.1)	55 (8.0)	55 (8.0)
588°K (600°F)	46 (6.7)	51 (7.5)	55 (8.0)	55 (8.0)
Shear Strength				
R.T.	28 (4.0)	44 (6.4)	59 (8.6)	53 (7.7)
588°K (600°F)	25 (3.6)	32 (4.7)	44 (6.4)	42 (6.1)
Density, g/cc	1.462	1.487	1.554	1.544
Resin Content, % w/w	32.40	32.35	32.56	31.67
Fiber Volume, % v/v	56.15	57.16	59.54	59.96
Void Volume, % v/v	7.96	6.40	2.12	2.99

(1) Pairs of composites, 1 and 2, 3 and 4, 5 and 6, and 7 and 8 were molded during the same autoclave run. The volatile matter from two laminates are thus represented by these weights.

TABLE 17   AUTOCLAVE MOLDING PROCESS STUDY ETHANOL/ DIGLYME SOLVENT SYSTEM (80/20 p.b.w.).

	A-1	A-2	A-3	A-4
Cure Cycle Number				
Composite No.	4	2	6	8
Dwell Temperature °K (°F)	353 (175)	408 (275)	353 (175)	353 (175)
Time, hour	16	1.5	16	16
Volatiles, g (1)	3.4	8.8	3.5	3.2
Dwell Temperature, °K (°F)	---	---	408 (275)	436 (325)
Time, hour	---	---	1.5	1.5
Volatiles, g	---	---	7.3	8.5
Total Volatiles Collected, g	12.0	11.5	12.8	12.8
Composite Properties				
Flexural Strength, MPa (Ksi)				
R.T.	386 (56)	786 (114)	814 (118)	841 (122)
588°F (600°F)	352 (51)	490 (71)	531 (77)	670 (97)
Flexural Modulus, MPa (Ksi)				
R.T.	43 (6.2)	57 (8.3)	54 (7.9)	54 (7.9)
588°K (600°F)	44 (6.4)	56 (8.2)	54 (7.9)	56 (8.2)
Shear Strength				
R.T.	24 (3.5)	45 (6.5)	50 (7.3)	56 (8.2)
588°K (600°F)	16 (2.3)	33 (4.7)	38 (5.5)	44 (6.4)
Density, g/cc	1.400	1.522	1.540	1.552
Resin Content, % w/w	31.55	28.75	31.23	32.66
Fiber Volume, % v/v	54.43	61.62	60.18	59.37
Void Volume, % v/v	12.12	5.24	3.38	2.24

(1) Pairs of composites, 1 and 2, 3 and 4, 5 and 6, and 7 and 8 were molded during the same autoclave run. The volatile matter from two laminates are thus represented by these weights.

5-11

TABLE 18   AUTOCLAVE MOLDING PROCESS STUDY METHANOL SOLVENT (PMR-15 CONTROL).

Cure Cycle Number	A-1	A-3
Composite No.	11	10
Dwell Temperature °K (°F)	353 (175)	353 (175)
Time, hour	16	16
Volatiles, g	3.9	3.5
Dwell Temperature, °K (°F)	---	408 (275)
Time, hour	---	1.5
Volatiles, g	---	1.2
Total Volatiles Collected, g	4.9	5.2
Composite Properties		
Flexural Strength, MPa (Ksi)		
R.T.	896 (130)	986 (143)
588°F (600°F)	648 (94)	710 (103)
Flexural Modulus, MPa (Ksi)		
R.T.	57 (8.2)	61 (8.9)
588°K (600°F)	59 (8.5)	63 (9.1)
Shear Strength		
R.T.	57 (8.2)	63 (9.2)
588°K (600°F)	40 (5.8)	45 (6.5)
Density, g/cc	1.539	1.597
Resin Content, % w/w	34.57	30.92
Fiber Volume, % v/v	57.23	62.68
Void Volume, % v/v	2.5	-0.1

of these volatile products was probably the
same, *i.e.*, water and methanol. This implies
that this dwell for 16 hours at $353^{\circ}K$ ($175^{\circ}F$)
removed only a small proportion of the tackifier,
diglyme. Separation of the components of the vola-
tile matter collected during the processing of
laminate 12 (Table 20, Section 5.2.2) by gas
chromatograph verified this observation. A
summation of this analysis is given in Table 19.

TABLE 19. ANALYSIS OF VOLATILE MATTER
AUTOCLAVE LAMINATE NUMBER 12[1]

	Fraction 1	Fraction 2
Methanol Concentration, % W/W	56	20
Diglyme Concentration, % W/W	44	80

[1] Gas chromatogry was used to separate and quantify
the relative amounts of these volatile products.
Analysis for water was not performed.

● The vapor pressure maintained over the laminates
in these lay-ups (0.5 mm Hg) was much lower than
the equilibrium vapor pressure of diglyme at this
temperature $353^{\circ}K$ ($175^{\circ}F$). Thus the removal of
diglyme at these temperatures was probably being
retarded by its relatively slow diffusion rate
through the laminates.

In summary these observations indicate that, under vacuum bag pro-
cessing conditions of improved tack PMR prepreg, substantial amidization
and imidization probably occurs prior to the removal of the majority of
the tackifier, diglyme.

TABLE 20 AUTOCLAVE MOLDING PROCESS
STUDY HOT MELT SYSTEM
(METHYL ESTERS).

Cure Cycle Number	A-3	A-5
Composite No.	9	12[1]
Dwell Temperature, °K (°F)	353 (175)	353 (175)
Time, hour	16	16
Volatiles, g	3.0	3.2
Dwell Temperature °K (°F)	408 (275)	422 (300)[2]
Time, hour	1.5	2.0
Volatiles, g	5.5	6.3
Dwell Temperature, °K (°F)	---------	477 (400)
Time, hour	---------	2.0
Volatiles, g	---------	0.8
Total Volatiles Collected, g	9.2	10.5
Composite Properties		
Flexural Strength, MPa (Ksi)		
R.T.	861 (125)	765 (111)
588°K (600°F)	593 (86)	510 (74)
Flexural Modulus, MPa (Ksi)		
R.T.	62 (9.0)	56 (8.1)
588°K (600°F)	61 (8.9)	51 (7.4)
Shear Strength		
R.T.	52 (7.6)	39 (5.6)
588°K (600°F)	37 (5.3)	31 (4.5)
Density, g/cc	1.574	1.438
Resin Content, % w/w	29.61	33.52
Fiber Volume, % v/v	62.94	54.32
Void Volume, % v/v	1.7	9.2

(1) Molded using vacuum bag pressure only, 97 KPa (14 psi)

(2) Actual cure cycle (Number A-5) employed a slow heating rate, 0.5°K (1°F)/min, up to
477°K (400°F). Volatile matter was collected upon reaching 422°K (300°F) and
477°K (400°F).

The data presented in Tables 16 through 18 indicates that the quality of the laminates fabricated in this study was highly dependent upon the cure cycle which was employed. However, by employing dwell cycles in the $408^\circ K$ ($275^\circ F$) to $436^\circ K$ ($325^\circ F$) range for one and one half hours, after a dwell cycle of 16 hours at $353^\circ K$ ($175^\circ F$) it was possible to fabricate relatively high quality laminates using the improved tack PMR system. These laminates exhibited mechanical properties equivalent to those of compression molded fabric laminates, $i.e.$, 41 PMa (6 Ksi) to 48 MPa (7 Ksi) short beam shear strength when tested at $588^\circ K$ ($600^\circ F$). Visual examination of these highest quality laminates, up to 100X magnification, did not reveal any appreciable void content. However, acid digestion of sections of these laminates indicated that they did have void contents ranging from 2% to 3% v/v. These are slightly higher than those found for the compression molded fabric laminates. There was no noticeable difference in processability between the two improved tack PMR systems.

To get an indication of the relative autoclave processability of the improved tack PMR system compared to the conventional PMR-15 system, two PMR-15 laminates were fabricated using cure cycles A-1 and A-3 (Figures 21 and 23 respectively). The void contents of the improved tack PMR laminates (methanol/diglyme solvent system) and the PMR-15 control laminates resulting from the use of these cure cycles are shown in Figure 25. This illustrates that there was a wider processing window using the PMR-15 control prepreg. That is, lower void volume laminates were obtainable using the PMR-15 control system, over a wider range of processing cycles, than were obtainable using the improved tack PMR system. However, since this was a brief screening study, it is very likely that higher quality improved tack PMR laminates would be obtained upon further process optimization.
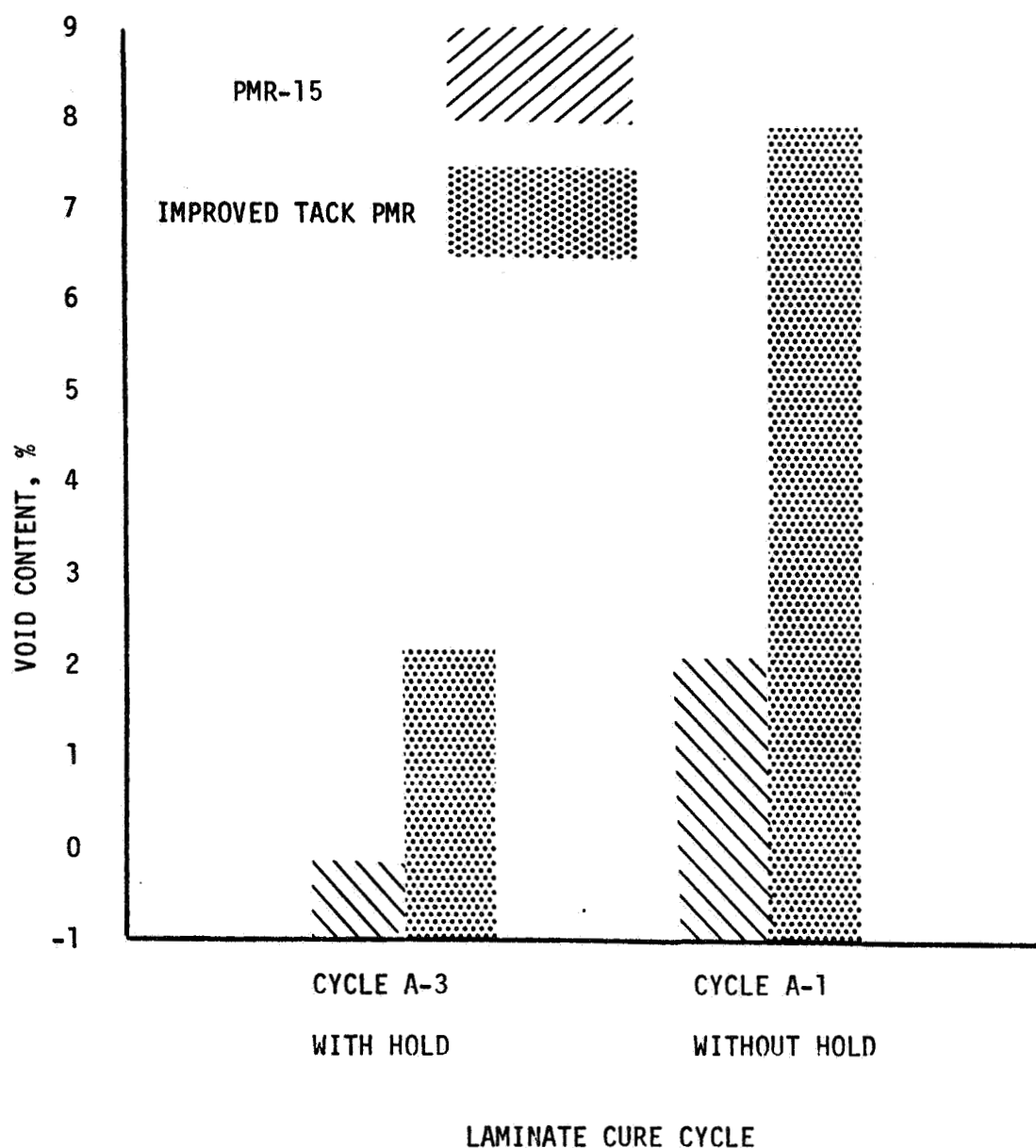
Figure 25 Void Contents of Improved Tack PMR and PMR-15
Laminates Fabricated in the Autoclave Using
Cure Cycles With and Without an Intermediate
Dwell Step.

5.2 HOT MELT COATED PREPREG EVALUATION

Additional laminates have been processed and evaluated from prepreg which has been preprared by hot melt coating techniques. The preparation of the high solids resin and prepreg used in this evaluation was discussed in Sections 3.2.1 and 3.2.2. The hot melt prepreg used in this study was prepared from a PMR formulation based upon the dimethyl ester of BTDA prepared in diglyme, NE and MDA in the molar ratios of 2.087 : 2.00 : 3.087.

5.2.1 LAMINATE PROCESSING

The processing of laminates in this study was based upon observations made during the autoclave molding of solution coated fabric prepreg (Section 5.1). Cure cycle A-3 (Figure 23) which produced the highest quality laminate from prepreg employing the methanol/diglyme tackifier was used to fabricate one laminate. In addition, a cure cycle which employed vacuum bag pressure only, 97 KPa (14 psi), for composite consolidation was screened. This cure cycle, number A-5 (Figure 26), employed a slow, steady heating rate during the imidization portion of the cycle. This was intended to minimize the amount of voids formed through this step so that upon rapid heating, from 477°K (400°F) to 588°K (600°F) only a small amount of resin flow would be necessary to affect adequate laminate consolidation.

5.2.2 LAMINATE EVALUATION

The mechanical and physical properties of the two laminates fabricated in this study are shown in Table 20. The properties of the laminate fabricated with 1.4 MPa (200 psi) autoclave pressure (composite number 9, Table 20) were nearly identical to the properties of laminates processed in a similar manner from solution coated fabric prepreg. There was a slight reduction of the shear strengths of the laminate employing the hot melt prepreg; however, this might be due to the relatively low resin content, 29.61% w/w, of this laminate.
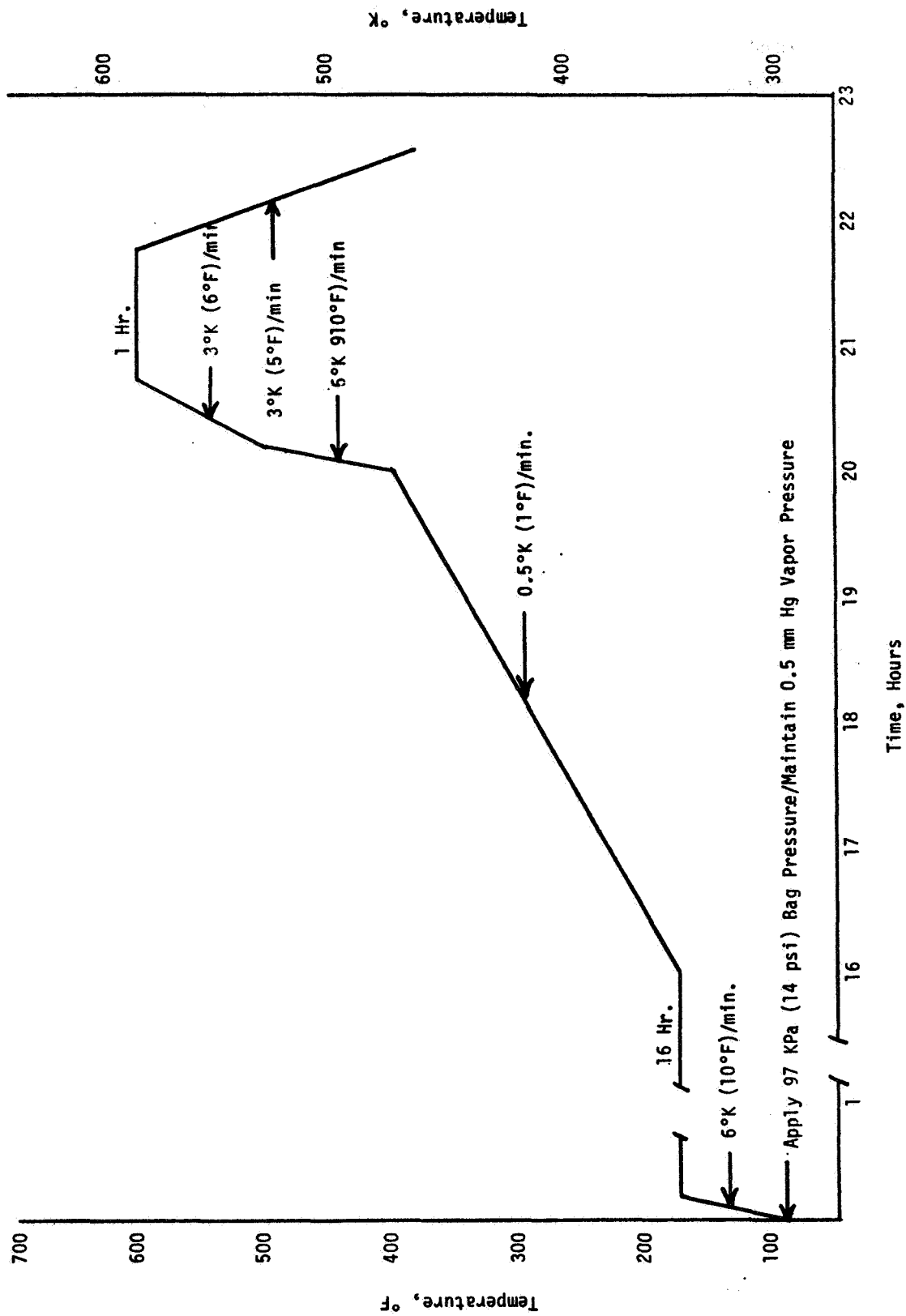
Figure 26 Autoclave Cure Cycle A-5.

5-18

The potential of using vacuum bag pressure only, 97 Kpa (14 psi). to process improved tack PMR fabric laminates was evaluated with composite number 12 (Table 20). The mechanical properties of this laminate were relatively low; this could be directly attributable to the rather high void content of the laminate. Microscopic examination of polished cross sections of this laminate showed that incomplete resin consolidation occurred in the resin rich interstitial regions between the tows of fibers. This characteristic could most likely be attributed to insufficient resin flow and not to void formation caused by the rapid evolution of volatile matter. As indicated by the amounts of volatile matter collected during the processing of this laminate, volatile evolution was essentially complete upon the laminate reaching $422^{o}K$ ($300^{o}F$). Optimization of this cycle, so that rapid heating would be affected from $422^{o}K$ ($300^{o}F$) to $588^{o}K$ ($600^{o}F$), could result in much higher resin flow and a higher quality laminate.

In summary, the autoclave fabrication studies performed on this program have identified process cycles that show promise for molding improved tack PMR-15 prepreg containing diglyme. However, as is a common occurrence, diglyme appears to be a good to excellent solvent for the PMR constituent compounds and prepolymer, thus it is very difficult to remove completely in order to avoid no to low void laminates. For those installations possessing equipment where long dwell cycles and rapid heat-up rates are easily controlled, use of a high boiling tackifier solvent component such as diglyme may be acceptable. However, for routine fabrication of large composite parts in conventional autoclave equipment in which narrow process envelopes are unacceptable, the cosolvent component approach to achieving tack, drape, etc. is most probably unacceptable.

6.0 CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions and recommendations reached during this program to develop PMR-15 prepregs with improved handleability and tack characteristics.

6.1 CONCLUSIONS

The incorporation of a fugitive solvent, dimethoxy ethyl ether, into the conventional PMR-5 resin formulation greatly increased the tack and handleability characteristics of prepregs prepared from this polyimide system.

- Improved tack PMR formulations, amenable to hot melt processing techniques, were developed which were alcohol free.

- Compression and autoclave molding processes were developed which repeatedly produced laminates, of up to 21.6 cm x 21.6 cm x 0.23 cm (8.5 in. x 8.5 in. x 0.09 in.) in dimension, of high physical and mechanical properties.

- Autoclave processing methods, which employed volatile removal in the $405^{\circ}K$ ($275^{\circ}F$) - $436^{\circ}K$ ($325^{\circ}F$) range, yielded improved tack PMR laminates of low void volume. This was realized by utilizing a maximum autoclave pressure of 1.4 MPa (200 psi).

6.2 RECOMMENDATIONS

Because of the recent finding which indicated that the auto-ignition temperature of diglyme is $\sim464^{\circ}K$ ($375^{\circ}F$) instead of the previously reported $>811^{\circ}K$ ($>1000^{\circ}F$), it is recommended that no further consideration be given to this compound as a tackifier for PMR-15 or any other high performance resin requiring solvent evaporation temperatures $>422^{\circ}K$ ($300^{\circ}F$).

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APPENDICES

A.   TEST PROCEDURES FOR CHARACTERIZATION
                          OF PREPREG HANDLEABILITY

A.1 TACK

The tack test involved the preparation and test of a single lap
shear type tensile specimen. Two 1 x 4 inch strips (warp parallel to
4 inch length) of prepreg were assembled with a one-inch overlap. A
dead weight of three pounds (3 psi) was placed over the lap joint for
60 seconds. The specimen was then pulled to failure using an Intrusion
Universal Test Machine at a strain rate of 5 inches per minute. Tack
was quantitatively defined as the average shear stress at failure,
which was given by the expression,

$$T = P/_A$$

where,

T = tack, kPa (psi)
P = load, N (lb)
A = area, M^2 (in^2)

A.2 VOLATILE CONTENT

Volatile content of graphite prepreg was determined by thermally
treating a tarred sample for 30 minutes at 477^OK (400^OF). After cooling
to R. T., the specimen was reweighed and the volatile content was cal-
culated by the following formula:

$$\text{Volatile Content} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 = Weight Sample

W_2 = Weight Sample After Heat Aging

A.3 DRAPE

Drape is a simpler parameter to consider and is less critical in assembly operations. As long as the prepreg can be conformed to the required contours without cracking or powdering resin, the material is felt to have adequate drape.

A simple approach to evaluating drape is to bend the room temperature prepreg over on itself and to crease it with finger pressure. This is perhaps a severe test and is sometimes modified by folding the material over a quarter or half inch diameter rod as a criterion. For purposes of this program, the fold and crease approach was used. Drape was qualitatively reported as,

  E = Excellent (very pliable)
  G = Good
  F = Fair
  S = Stiff
  C = Cracking

B. PROCEDURES FOR THE ISOTHERMAL GRAVIMETRIC ANALYSIS OF BULK RESIN AND COMPOSITE SAMPLES

The test specimens were placed in a ventilated chamber which had a volume of 14 liters, this, in turn, was placed in a forced air oven. This inner chamber was fitted with a coiled metal tube which was placed at the bottom of the chamber. Air was metered through the tube which had holes drilled at 2.5 cm (1 in.) intervals. A flow rate of 100 ml/min was maintained with a calibrated flowmeter. Bottled dry air was employed for all aging studies. The temperature inside the chamber was constantly monitored with Hewlett Packard 680 strip chart recorder and held at $588^{\circ}K$ ($600^{\circ}F$) $\pm$ $2.5^{\circ}K$ ($5^{\circ}F$).

C. THERMAL MECHANICAL ANALYSIS OF BULK RESIN AND COMPOSITE SAMPLES

Bulk resin and matrix glass transition temperatures were determined with a DuPont Thermomechanical analyzer. An expansion probe with a 5g load was used to measure the dimensional changes of the sample.

A-2

The samples were heated at a rate of 10^OK/min while under a nitrogen atmosphere.

The glass transition temperature was defined as the temperature at which there was a marked increase in the expansion rate of the sample. This was estimated by drawing tangents to the initial (glassy state) expansion curve and the next definable expansion curve. The intersection of these tangents was taken as the glass transition temperature.

A representative TMA profile determined in this work is given in Figure C-1.

D. TEST PROCEDURES FOR CHARACTERIZATION OF PREFORMS AND COMPOSITES

D.1 PREFORM EXTENT OF VOLATILE EXPULSION

The extent of volatile expulsion from the oven imidized preforms was a measure of the relative volatile content of the preforms compared to the volatile content of single plies of prepreg. Preforms and plies of prepreg always came from the same batch. The volatile content of the preforms was determined by following the procedure given in Appendix A.3. The relative extent of volatile expulsion was defined as,

$$\text{Volatile Expulsion} = \frac{V_{pf}}{V_{pp}} \times 100$$

where,

V_{pf} = preform volatile content

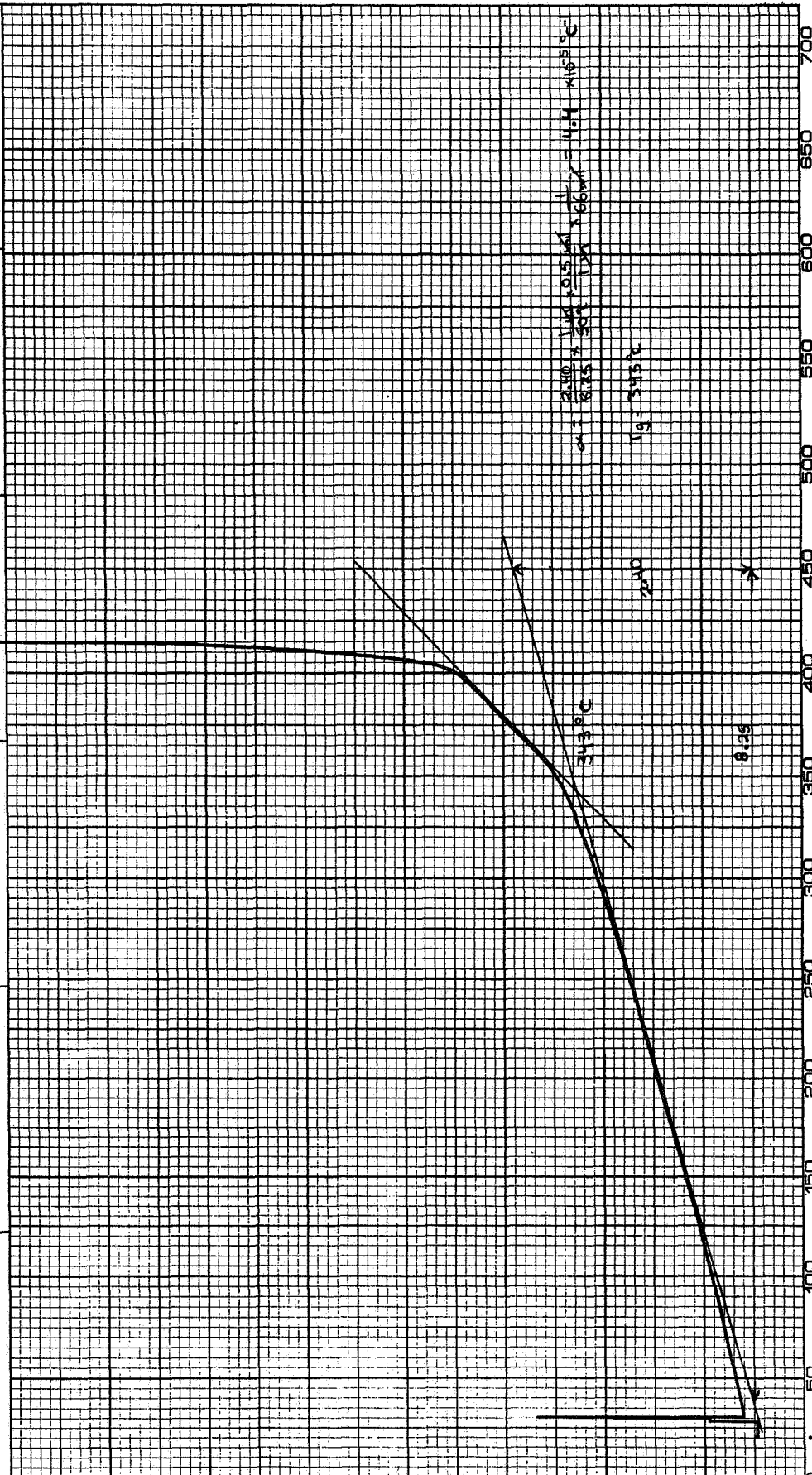V_{pp} = prepreg volatile content

D.2 COMPOSITE CHARACTERIZATION

The following tests were used to quantitatively define laminate physical and mechanical properties.

D.2.1 RESIN FLOW

Resin flow during the molding of laminate was defined as,

TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure C-1. TMA of MOLDING 881-38

$$\text{Resin Flow} = \frac{W_2}{W_1}$$

where,

W_1 = Total laminate weight after molding

W_2 = Weight of resin flash

D.2.2 RESIN CONTENT

The resin was digested from the cured sample by pouring acid (concentrated H_2SO_4) onto the sample in a glass beaker and then heating the acid until it turned black. At this point, 30% hydrogen peroxide solution was added dropwise to the acid until it turned clear again. The acid was reheated for a minimum of one hour. During this period, further drops of hydrogen perioxide solution were added to clear the acid whenever the acid turned black. After the solution remained clear for at least one half hour it was cooled to room temperature. The acid was decanted from the filaments using a fritted glass filter, washed first in distilled water and then acetone, after which the filaments were dried for 15 minutes in a $450^{\circ}K$ ($350^{\circ}F$) air circulating oven. Resin solids contents were calculated:

$$W_r = \frac{(W_1 - W_2)}{W_1} \times 100$$

Where,

W_r = Weight Content of Resin Solids, % w/w

W_1 = Weight of Cured Composite Sample

W_2 = Weight of Filaments after Acid Digestion of the Resin Matrix

D.2.3 DENSITY OF COMPOSITES

Specific gravity of composites was determined by weighing specimen in air and in water. Specific gravity was calculated by the formula:

$$\text{Specific Gravity} = \frac{W_A}{(W_A - W_W)} \times 100$$

Where:

W_A = Weight Sample in Air

W_W = Weight Sample in Water

D.2.4 Composite Fiber Volume

Fiber volume percent of the composites was calculated by the formula:

$$V_f = 100 \ (1-K) \ \frac{D_C}{D_f}$$

Where:

V_f = Volume Percent Fiber, %

D_C = Measured Density of Composite, g/cm^3

D_f = Density of Fiber, g/cm^3 (assumed to be 1.76 g/cm^3)

K = Weight Fraction, Resin

The specific gravity of the Celion fibers was assumed to be 1.76 g/cm^3.

D.2.5 COMPOSITE VOID CONTENT

Void contents of the composites were calculated using the formula:

$$V_v = 100 - D_C \left(\frac{W_r}{D_r} + \frac{W_f}{D_f} \right)$$

Where:

V_v = Volume of Voids, % v/v

D_C = Measured Density of Composite, g/cm^3

D_r = Density of Resin, g/cm^3 (assumed to be 1.36 g/cm^3)

$$D_f = \text{Density of Fiber, g/cm}^3$$

$$W_r = \text{Weight Content of Resin, \%}$$

$$W_f = \text{Weight Content of Fiber, \%}$$

D.2.6 SHEAR STRENGTH OF COMPOSITES

The cured composites were machined into short beam shear specimens 0.64 cm (0.25 in.) wide and 1.52 cm (0.60 in.) long and tested in flexure using a 4:1 span to depth ratio. Loading rate was 0.13 cm/min (0.05 in/min)·

Shear strengths were calculated using the simple formula:

$$S_u = \frac{0.75V}{tb}$$

Where:

$$S_u = \text{Ultimate Shear Strength, MN/m}^2 \text{ (lb/in}^2\text{)}$$

$$V = \text{Load at Failure, N (lb)}$$

$$t = \text{Specimen Thickness, m (in)}$$

$$b = \text{Specimen Width, m (in)}$$

D.2.7 FLEXURAL PROPERTIES OF COMPOSITES

The cured composites were machined into flexural specimens 1.27 cm (0.5 in) wide by 10 cm (4 in) long and tested in flexure, using three point loading, and a 32:1 span-to-depth ratio. Loading rate was 0.13 cm/min (0.05 in/min).

Flexural strengths and moduli were calculated using the formulae:

$$F_u = \frac{3PL}{2bd^2}$$

$$\text{and} \quad E_b = \frac{L^3 m}{4bd^3}$$

Where:

F_u = Stress in the Outer Fiber at Mid-span, MN/m^2 (lb/in^2)

E_b = Modulus of Elasticity in Bending, GN/m^2

P = Load at Failure, N (lb)

L = Span, m (in)

b = Width of Specimen, m (in)

d = Thickness of Specimen, m (in)

m = Slope of the Tangent to the Initial Straightline Portion of the Load Deflection Curve, N/m (lb/min)

E. METHODS FOR GPC ANALYSIS

The GPC (Gel Permeation Chromatography) analysis was performed with Waters Associates' $60A^0$ μ Porasil GPC columns. The conditions of analysis are listed in Table E-1. The method of analysis was identical to that reported by K. E. Reed (Reference 6). The elution volume and peak area integration was performed by a Spectra-Physics 4000 microprocessor.

Table E-1. GPC ANALYSIS

GPC Columns	- 3-60A^0 μ Porasil
Solvent	- Water/Methanol (1:1 Ratio) Methanol - Burdick and Jackson Water - Baker HPLC
Detector	- DuPont Variable Wavelength Ultraviolet Spectrophotometer set at 254 nm
Flow	- 1.0 ml/min
HPLC	- DuPont Model 850
Temperature	- 40^{0}C
Automation	- Spectra-Physics 4000

A representative Chromatograph of the solutions analyzed during this program is given as Figure E-1.

CHANNEL 1   RUN 18   FILE 3   METHOD G

INDEX 18

PEAK #	AREA %	RT	AREA
1	97.04	302	540322 S
2	2.963	343	16498 /
TOTALS	100		556820

Figure E-1. GPC 50% w/w BTDE in METHANOL, FRESH

F.   ULTRASONIC C SCANS OF UNIDIRECTIONAL LAMINATES

The ultrasonic C scans of representative laminates evaluated in the development oc composite properties, Section 4.0, are presented below:
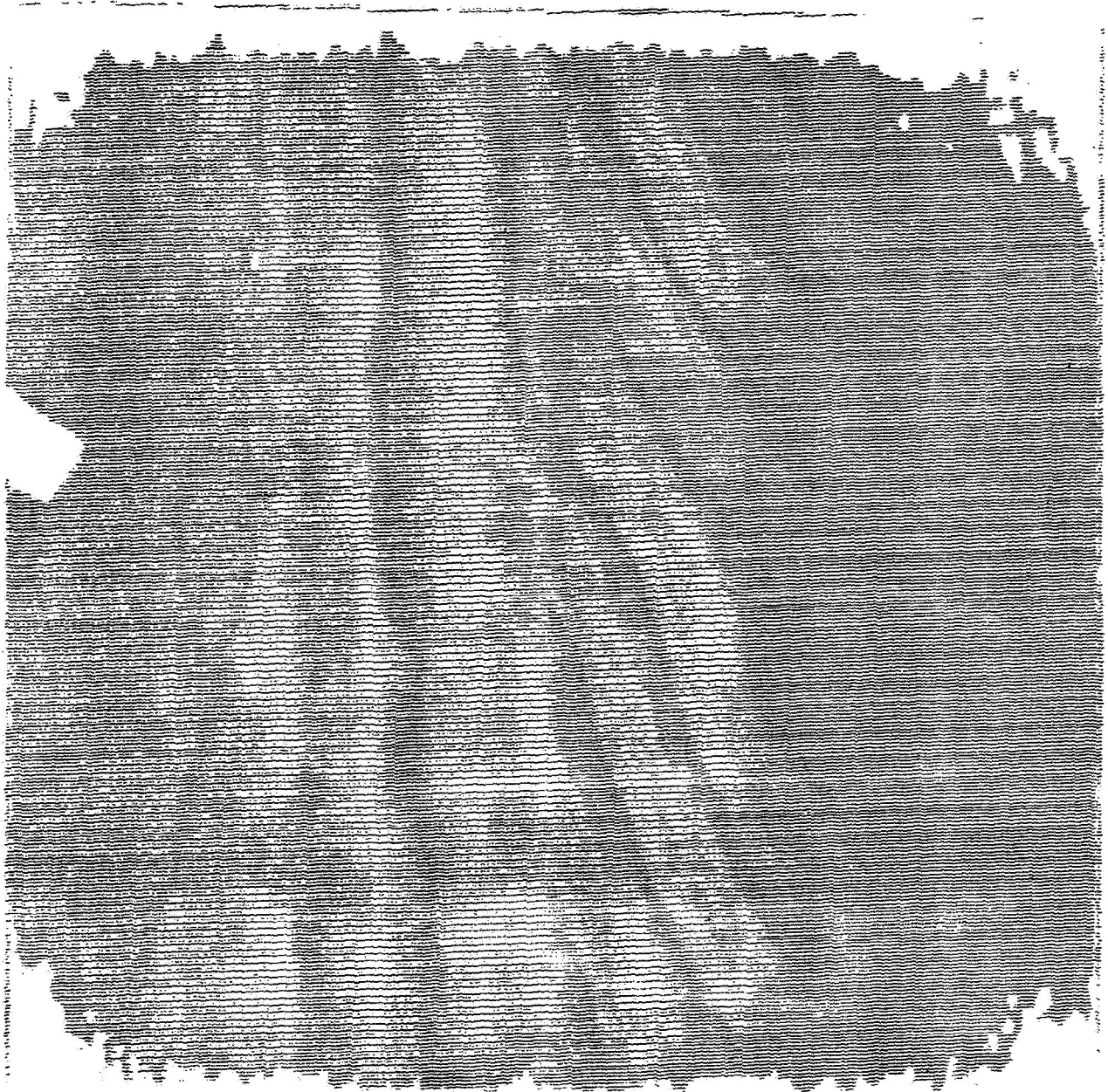
Figure F-1.   C-SCAN OF PMR-15
CONTROL (LAMINATE L8)
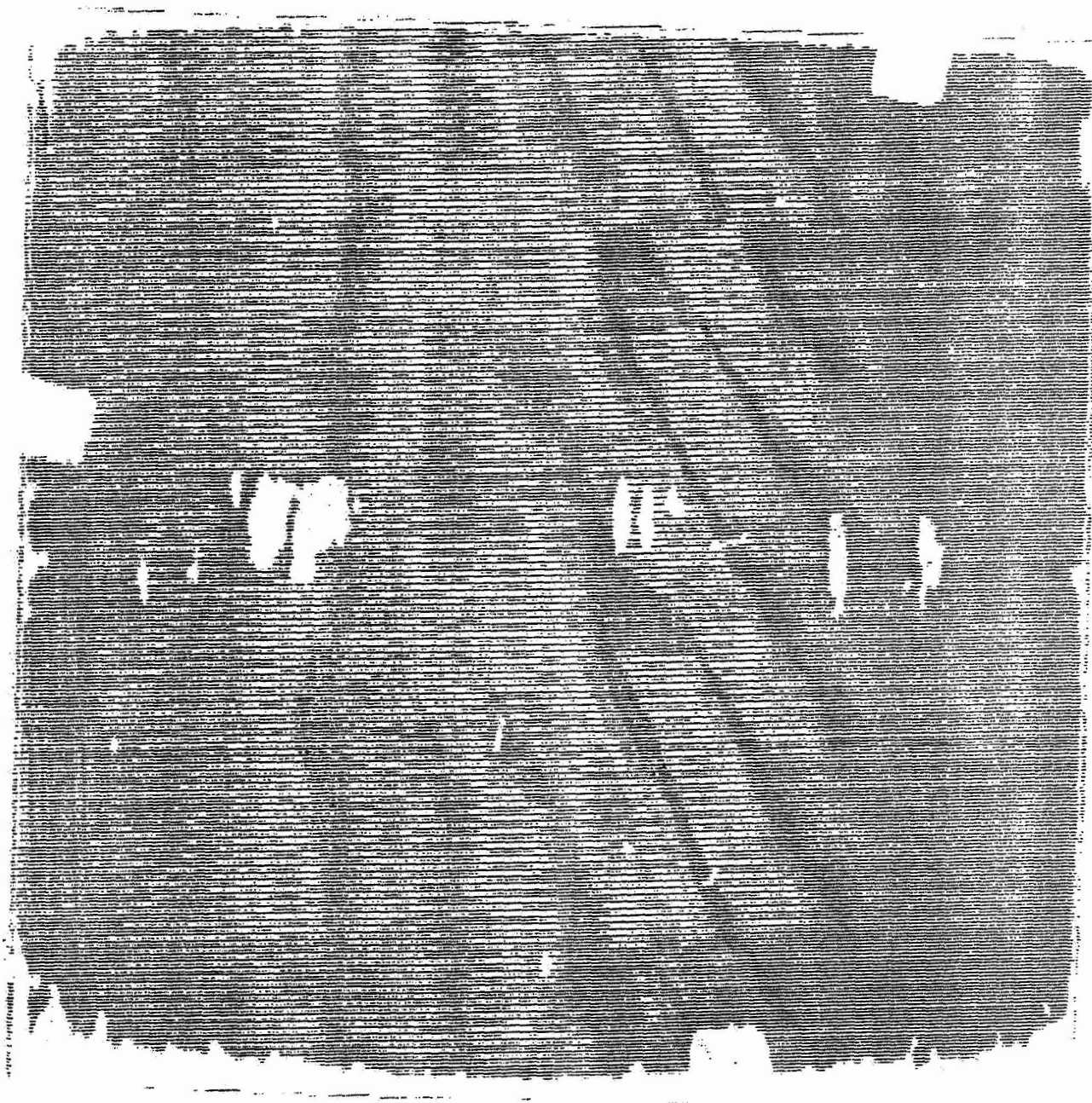
Figure F-2.   C-SCAN OF LAMINATE 9
             FABRICATED FROM FRESH PREPREG
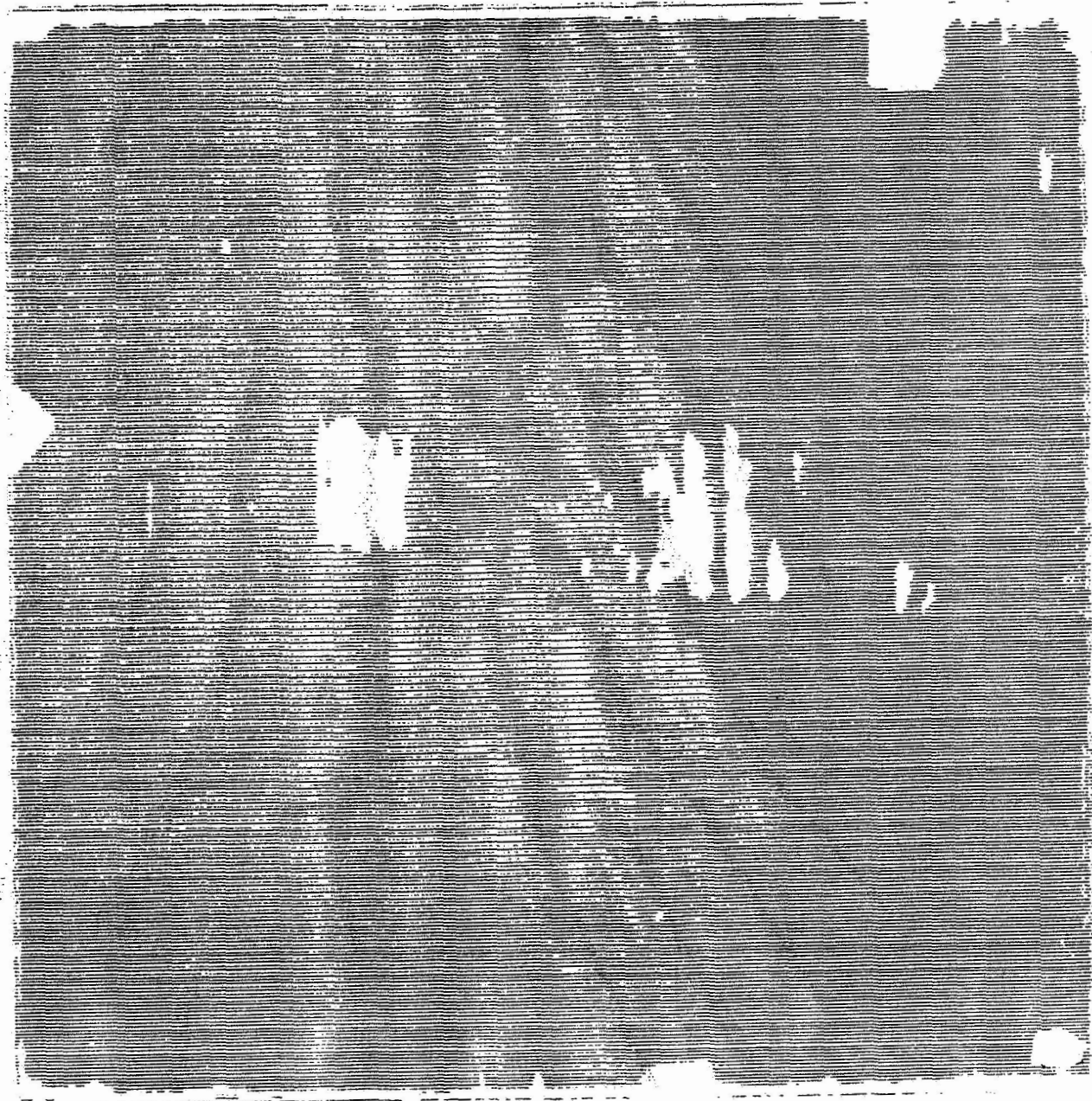
Figure F-3.   C-SCAN OF LAMINATE 12 FABRICATED FROM
PREPREG AGED 30 DAYS AT 278°K (40°F

A-12
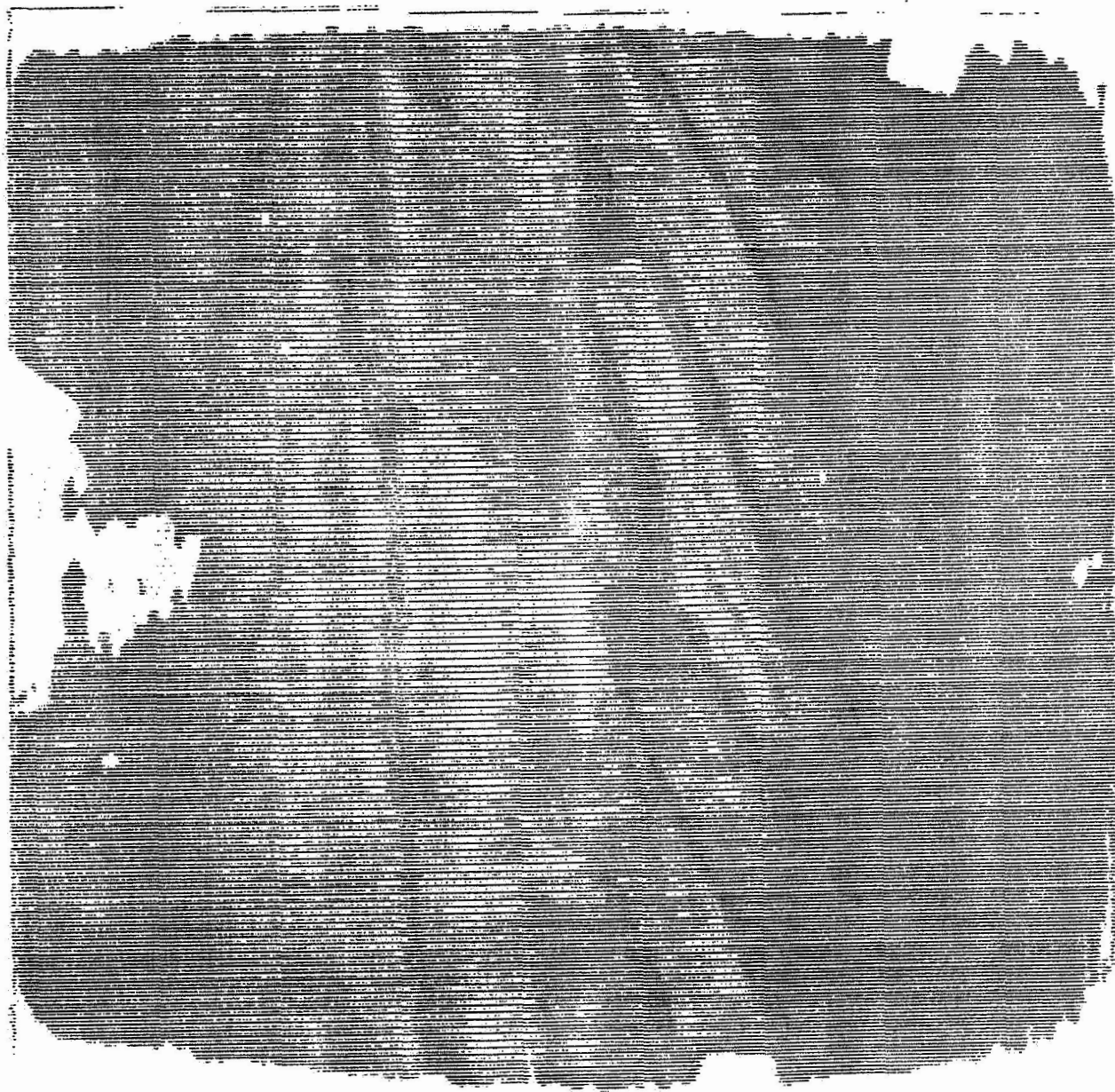
Figure F-4. C-SCAN OF LAMINATE 10 FABRICATED FROM
PREPREG AGED 14 DAYS AT R.T.
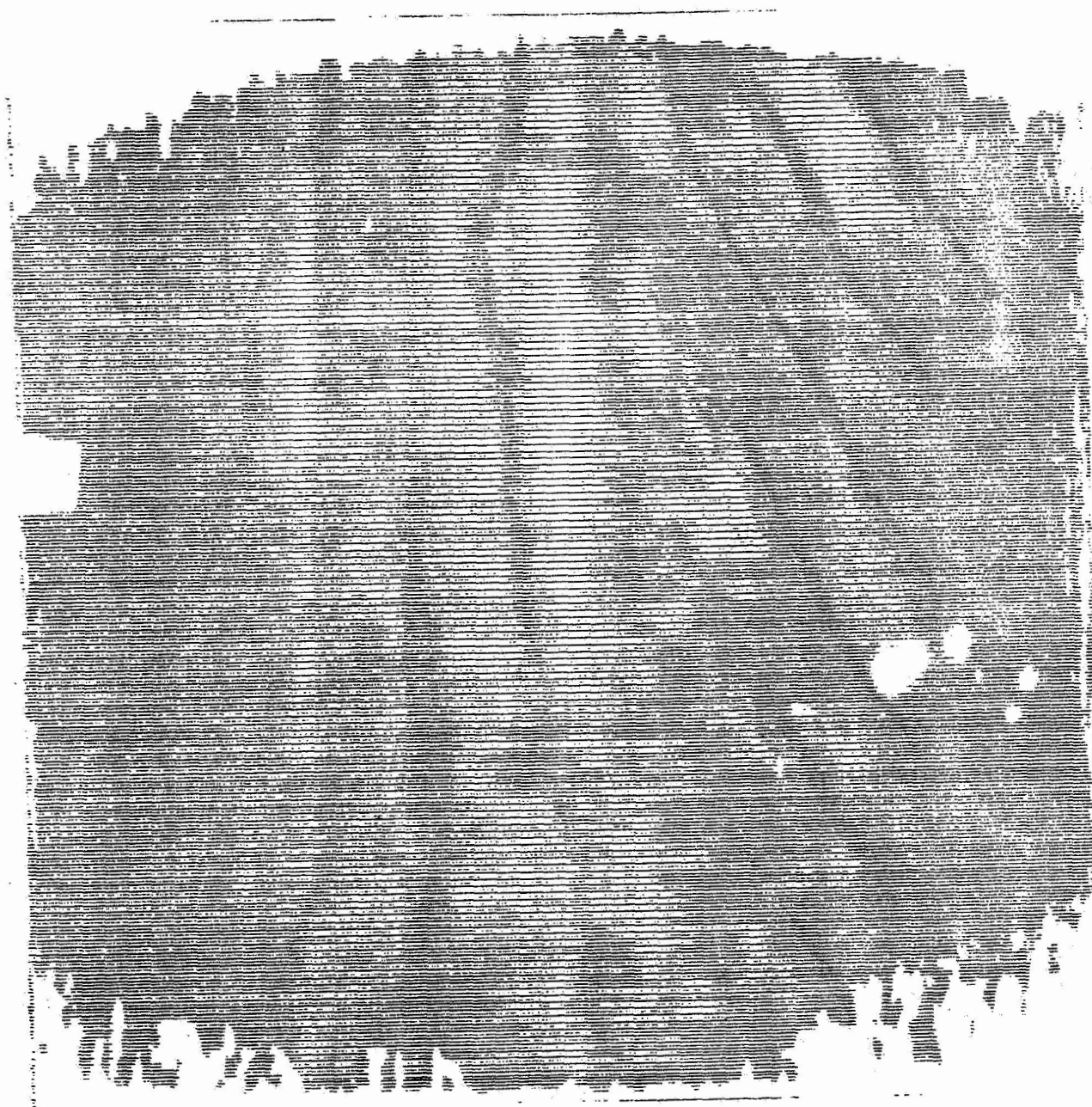
Figure F-5. C-SCAN OF LAMINATE 16 FABRICATED FROM PREPREG AGED
30 DAYS AT 278°K AND 14 DAYS AT R.T.

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